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DEVELOPMENT OF LACTIC AND SUCCINIC ACID BIOREFINERY CONFIGURATIONS FOR INTEGRATION INTO A THERMOMECHANICAL PULP MILL

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Ce mémoire intitulé:

DEVELOPMENT OF LACTIC AND SUCCINIC ACID BIOREFINERY CONFIGURATIONS FOR INTEGRATION INTO A THERMOMECHANICAL PULP MILL

présenté par : LEE Hana

en vue de l'obtention du diplôme de : Maîtrise ès sciences appliquées

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DEDICATION

To my parents,

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RÉSUMÉ

L'augmentation des émissions de CO_2 et la diminution des ressources énergétiques d'origine fossile ont provoqué une augmentation de l'intérêt porté à la production de carburants et de produits chimiques biobasés ces dernières années. En même temps, le secteur des pâtes et papiers, qui était l'un des moteurs de l'industrie canadienne, a été confronté à une crise qui a été provoquée par un haut prix de l'énergie, une concurrence accrue de la part des pays en développement et une diminution de l'utilisation du papier.

La bioraffinerie verte intégrée (BRVI), qui consiste à coupler une usine de pâtes et papiers existante à une nouvelle usine de production de produits chimiques de valeur, est apparue comme étant une solution permettant aux usines de pâtes canadiennes de redevenir compétitives grâce à la diversification de leur gamme de produits.

L'acide lactique et l'acide succinique sont des produits chimiques importants de par leur haut potentiel d'application dans les industries cosmétique, agro-alimentaire et pharmaceutique. Ils sont tous les deux obtenus par des voies technologiques pétrochimique ou biochimique. Cette dernière est basée sur la fermentation de sucres par des bactéries. Ces dernières années, la voie biochimique a reçu une attention croissante, car elle offre à l'industrie chimique l'opportunité de produire des produits chimiques verts.

La production économiquement compétitive de l'acide lactique et de l'acide succinique nécessite l'utilisation de sources de carbone diverses (telles que la biomasse lignocellulosique) et le développement de procédés viables. La bioraffinerie verte intégrée à une usine de pâte thermomécanique (*TMP*) produisant de l'acide lactique et de l'acide succinique biobasés permet non seulement l'échange de matière première mais également de chaleur. L'objectif de ce projet est de proposer les configurations de bioraffinerie de production d'acide lactique et succinique et de démontrer la faisabilité technique et la pertinence économique de la production d'acide lactique et d'acide succinique dans une bioraffinerie intégrée à une usine de pâtes thermomécanique.

Quatre modèles de simulation ont été développés sur Aspen Plus lors de ce projet : (i) la production d'acide lactique biobasé avec récupération du produit final par précipitation ou (ii) électrodialyse et (iii) la production d'acide succinique biobasé avec récupération par cristallisation directe et (iv) électrodialyse. L'intégration énergétique et la conception d'un réseau d'échangeurs de chaleur (Heat Exchanger Network, *HEN*) des installations de production d'acide lactique et succinique ont

été réalisées en se basant sur les résultats de simulation et des données fournies par FPInnovations. Des opportunités de réduction de la consommation des flux chauds ont été émises à partir des résultats obtenus précédemment. À la fin du projet, une analyse économique globale est effectuée en se basant sur les bilans de matière et d'énergie obtenus à partir des modèles développés.

ABSTRACT

In recent years, with rising concerns about CO_2 emission and depletion of fossil fuel, production of bio-based fuel or chemicals has attracted more attention. Meanwhile the pulp and paper industry, which used to be one of the major industries in Canada, has been confronted with a crisis in its operation during last two decades resulted from high energy price, competition with developing countries, and reduced paper demand.

As an alternative to this situation, the integrated forest biorefinery (IFBR), which is a concept of coupling of an existing conventional pulp and paper mill and a new plant for the production of valuable chemicals, has appeared as a potential way to make the Canadian pulp mills competitive again by diversifying their products.

Lactic acid and succinic acid are important chemicals due to their high potential for applications in the food, cosmetic, and pharmaceutical industry. Both lactic acid and succinic acid are produced by petro-chemical pathways or bio-chemical pathways, which are based on the fermentation of sugars by bacteria. In recent years, bio-chemical pathways have received increased attention as they offer an opportunity to the chemical industry to produce green chemicals.

So far, the bio-based lactic or succinic acid have been produced commercially from corn starch. This starch based raw material is converted to sugars by hydrolysis. Microorganisms produce lactic or succinic acid by metabolizing the sugars during the fermentation. Pure lactic and succinic acid are obtained by recovery from the fermentation broth.

Making lactic and succinic acid production economically competitive requires the use of various carbon sources (such as lignocellulosic biomass) as well as the development of viable processes. The integrated forest biorefinery (IFBR) that combines two or more processes of the production of pulp and paper and co-products such as bio-fuels or bio-chemicals allows not only the supply of raw material but also the transfer of heat. Before now many researches on the IFBR have been conducted into Kraft pulp mills as a receptor and relatively less study was done about Thermomechnical pulp (TMP) mills. The main objective of this project is to propose the configurations of biorefinery of production of lactic and succinic acid and to demonstrate the technical and economic feasibility of the integrated biorefinery composed of a TMP process and a lactic or succinic acid plant.

In this project four simulation models on Aspen Plus were developed: bio-based lactic acid production with the recovery by precipitation and electrodialysis, and bio-based succinic acid production with the recovery by direct crystallization and electrodialsys. With the stream data of stand-alone lactic and succinic plant extracted from the results of the simulations and the stream data of TMP mill provided from FPInnovations, heat integration was performed and Heat Exchanger Network was designed. From these results, heat recovery opportunities that indicate the reduction of external hot utility (steam) were estimated. At the end of this project, a simple economic evaluation was performed based on the material balance and energy use from the simulation models.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Area of heat exchanger
CC	Composite Curve
CTMP	Chemi-Thermomechanical Pulping
ΔT min	Minimum temperature difference
GCC	Grand Composite Curve
GDP	Gross Domestic Product
HEN	Heat Exchanger Network
HEX	Heat exchanger
HMF	Hydroxymethylfurfural
IEA	International Energy Angency
IFBR	Integrated forest biorefinery
LA	Lactic acid
LAB	Lactic acid bacteria
LP steam	Low pressure steam
NREL	National Renewable Energy Laboratory
P&P	Pulp and Paper
PLA	Poly lactic acid
RMP	Refiner Mechanical Pulping
SA	Succinic acid
SGW	Stone Ground Wood Pulping
SSF	Simultaneous Saccharification and Fermentation
TCA	Tricarboxylic acid
TMP	Thermomechanical Pulp

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CHAPTER 1 INTRODUCTION

1.1 Context

In the modern industrial society, the use of fossil resources such as coal, petroleum, and natural gas has provided the main power to operate our world. With the increase of transportation, electricity production, and industry in general, oil became the dominant fuel during the 20th century. The total petroleum consumption in Canada increased from 1,448 thousand barrels a day in 1983 to 2,431 thousand barrels a day in 2013 [1].

The development of a fossil-fuel-based economy has greatly improved our way of life but also raised some concerns like the depletion of fossil fuel, the high dependence on oil price, and the increase of political conflicts in the world. In addition, the combustion of fossil fuel emits gas such as CO_2, CH_4, NO_x and SO_x, which cause greenhouse effect and pollution. Thus, it is important to develop alternatives based on renewable energies.

On the one hand, the pulp and paper (P&P) industry in Canada has encountered a downswing in its traditional production on account of the decrease of paper use as well as the competition of low cost products from developing countries. Moreover, its large use of energy and water makes it hard to be operated in the long term. The conversion of an existing pulp and paper mill into an integrated forest biorefinery (IFBR), which produces value-added chemicals from lignocellulosic biomass and is able to substitute petroleum-based products, has been suggested as an alternative for the transformation of the industry.

The conversion of carbohydrates into ethanol fuel is a well-developed process. Almost all the bioethanol is currently produced from sugarcane or grain. The use of these raw materials has some disadvantages, for example, food shortage in developing countries, increase of the international price of grain and devastation of forests to increase agricultural land. Therefore, there is a need to develop the use of non-food resources in a biorefinery concept.

Besides bio-fuels there is also a strong demand for bio-based chemicals that can substitute petroleum-based chemicals. Lactic and succinic acids are promising candidates as products of the IFBR. They have been chosen between the top 12 value-added chemicals from sugars and syngas by the US Department of Energy, thanks to their various potential uses [2].

Lactic and succinic acid production from biomass consists of the following main steps: extraction and hydrolysis of sugars from various carbon sources (e.g. energy crops, lignocellulosic biomass, and agricultural residues), fermentation of sugars, and purification of the final product. So far, the main raw material for commercial production of biobased lactic and succinic acids are grain crops, which forms a large part of the total production cost.

It has been reported that the cost of feedstock of biobased Poly Lactic Acid (PLA) production is more than 34% of the entire manufacturing cost [3]. Therefore, making lactic and succinic acid economically competitive requires the use of various carbon sources such as lignocellulosic biomass as well as the development of economically viable processes.

From this point of view, the integration of a biorefinery in a Thermomechanical Pulping (TMP) mill is a good alternative to process sugars obtained from the wood components. Moreover, it is also important to reach high energy efficiency to make the biorefinery process competitive. Heat integration based on Pinch Analysis can be conducted to increase thermal efficiency of the biorefinery by analyzing interactions between processes. Heat sources are used to supply heat to the heat sinks minimizing the demand of external energy.

CHAPTER 2 LITERATURE REVIEW

2.1 Lignocellulosic biomass

Biomass is the living or recently living biological material including carbohydrates that can serve as a source of energy or chemicals. Lignocellulosic biomass is one of the most abundant materials in the world such as trees, agricultural food and residues, and pulp and paper mill residues [4]. As Canada has a large, well-developed forest that occupies 397.2 million ha, 41% of Canada's land area and 10% of the world's forested land, the utilization of wood has been considered as one of the country's important valuable resources [5].

Wood is mainly composed of cellulose, hemicelluloses, lignin, and extractives. Cellulose makes up about 45% of the dry weight of wood and forms long chains of glucose linked by β-1,4-glycosidic bonds [6]. Hemicelluloses make up 25~30 % of the dry weight of wood and are composed of several sugars such as xylose, mannose, galactose, glucose, and arabinose. The different sugars are linked to each other by β-1,4- and β-1,3-glycosidic bonds and form branch structures with short lateral chains. Lignin makes up 18~35 % and is the most abundant polymer in nature. It is an amorphous heteropolymer, water insoluble that protects the plant body from microbial attacks and oxidative stress. The structure of wood in a microscope scale is represented in Figure 2-1.

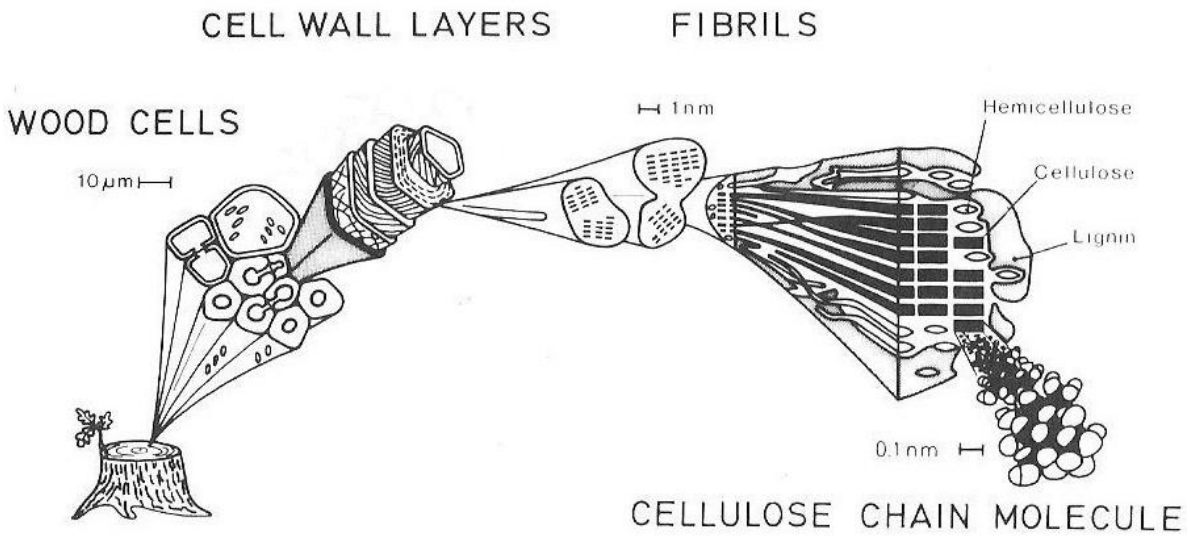


Figure 2-1 Structure of wood [7]

The composition of lignocellulosic biomass varies in the different plant species. For example, woody biomass contains more cellulose, whereas agricultural biomass (e.g. wheat straw) has more hemicelluloses. A comparison of compositions of different lignocellulosic biomass is shown in Table 2-1. The hardwood hemicelluloses are composed of higher fraction of pentoses than softwood hemicelluloses, which contain more hexoses [8].

Table 2-1 Composition of lignocellulosic biomass [8]

Lignocellulosic biomass	Cellulose (%wt.)	Hemicelluloses (%wt.)	Lignin (%wt.)
Hardwood	40-55	24-40	18-25
Softwood	45-50	25-35	25-35
Grasses	25-40	35-50	10-30
Wheat straw	30	50	15

2.2 The pulp and paper industry

2.2.1 The current state in Canada

The pulp and paper production in Canada has increased steadily of the last century, however, during the last 15 years the forest industry is in a declining tendency caused by U.S. recession of 2007-to-2009, the decrease of consumption of paper from the growth of the digital media and the global competition with developing countries (Figure 2-2) [9, 10].

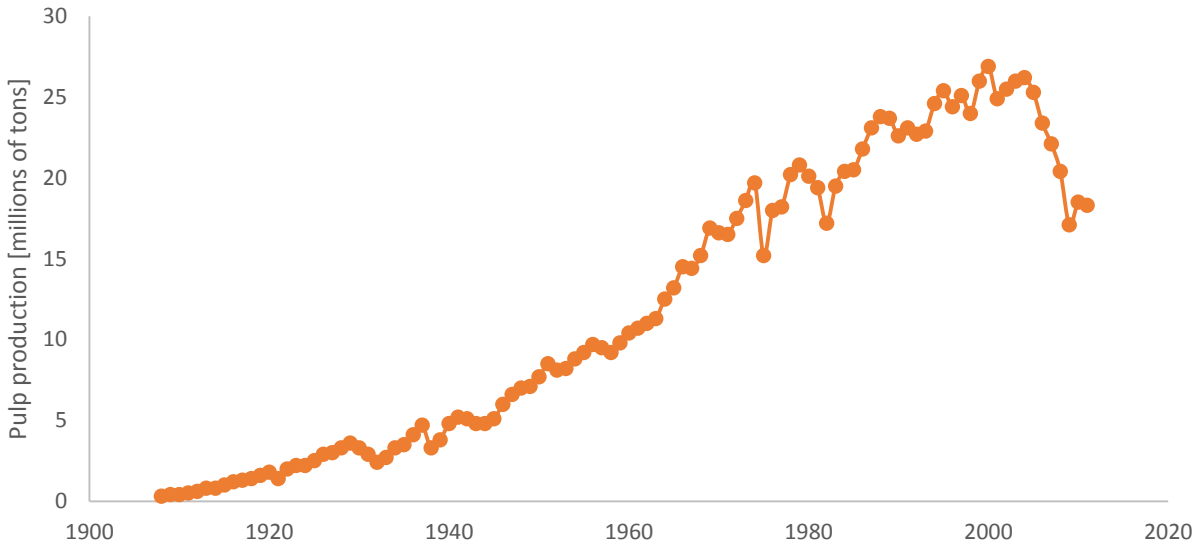


Figure 2-2 Pulp production in Canada [10]

As a consequence, the contribution of the pulp and paper industry to the gross domestic product (GDP) in Canada has been decreasing for the last decade (Figure 2-3). In 2013, forest products contributed $19.8 billion, which is 1.25 % of GDP in Canada, while pulp and paper product manufacturing accounted for 36% of the contribution of the forest sector [11].

In fact, several pulp and paper mills in Canada closed their operations over the past few decades: for example, Eurocan mill (Kitimat, BC, 2010), Resolute Forest Products Inc. (Fort Frances, ON, 2014), Laurentide mill (Shawinigan, QC, 2012) [12]. Therefore, it is necessary to develop an alternative approach for using forest biomass and maintain P&P mills in operation. In 2009, the Government of Canada launched “The Pulp and Paper Green Transformation Program”, with a funding of $90.4 million over four years in order to help pulp and paper mills to be more energy efficient, to degrease their greenhouse gases emissions and water waste, or to produce new bio-based products [13].

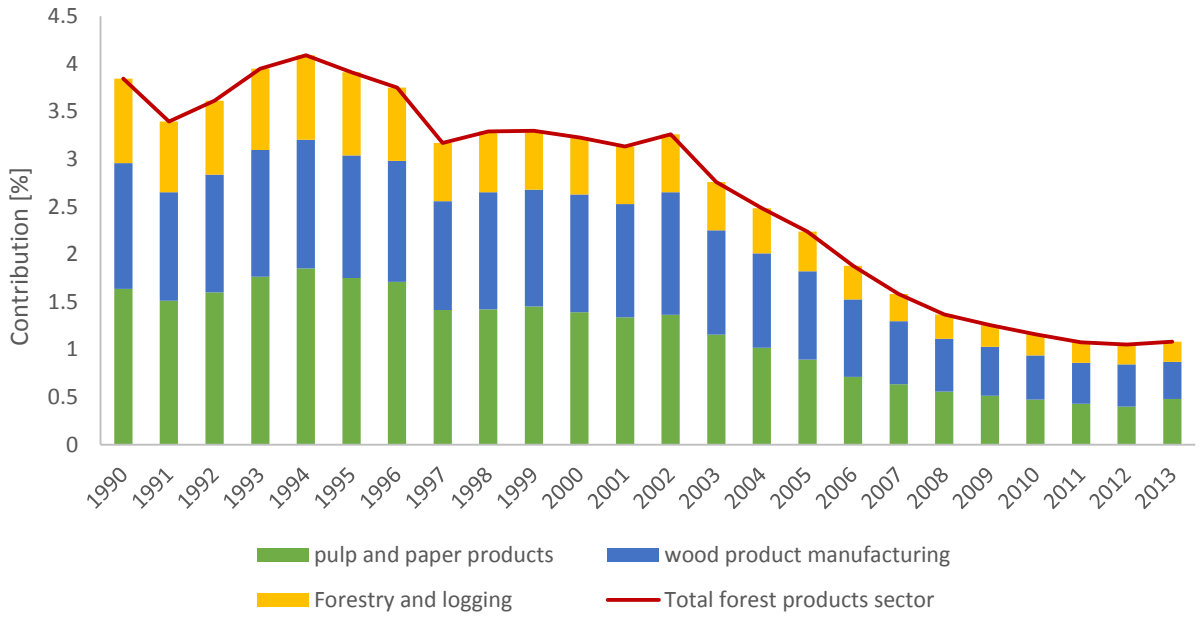


Figure 2-3 Forest products sector contribution to the GDP of Canada [14]

2.2.2 Pulping process

Pulping is the process of separating the fibrous mass (cellulose) from the other wood components (hemicelluloses and lignin) by rupturing the strong linkages within the wood structure. This task can be accomplished mechanically, chemically, or by combination of these two treatments.

As the oldest form of pulping, mechanical pulping separates fibers by mechanical energy. The main objective in the mechanical pulping is to separate the fibers from the lignin and suspend them in water for paper making. The advantage of mechanical pulping is a high yield of production (up to 90~95%) [15]. However, the fiber strength and the resistance to discoloration are low, because the mechanical pulping process does not dissolve lignin. Therefore, most of the mechanical pulp is used for lower grade papers such as newspaper and magazines. The main variations of the TMP processes are Stone Groundwood Pulping (SGW), Refiner mechanical Pulping (RMP), Thermomechanical Pulping (TMP), or Chemi-Thermomechanical Pulping (CTMP) [16].

The objective of chemical pulping is to separate and dissolve the lignin by cooking wood chips with chemicals under high temperature and pressure. The two main methods are the Kraft process (alkaline) and the sulphite process (acidic) [15].

2.2.2.1 Thermomechanical Pulping

TMP process is the most common mechanical process today. The TMP process produces the highest grade mechanical pulp but a large amount of energy is required due to the use of steam because of thermal pretreatment.

Basic flow diagram for the TMP process is shown in Figure 2-4. In the TMP process, wood chips are first steamed to make them soft before being grounded during the refining. It is important to conduct the refining at a temperature below 140 °C, if the refining is performed above 140°C, the fibres are easily separated but the lignin is also softened dramatically. With cooling this lignin reverts to a glassy state thus making hard to separate the fibres. The refining process causes the fibres to form a coiled shape that is termed 'Latency'. It is necessary to disintegrate this freshly produced fibres in hot water. A vigorous mixing at a temperature 71~93°C in a chest is conducted for the latency removal to produce paper. To maximize the average time in a chest of a given volume, it is preferable to have a long rectangular chest. The pulp produced by TMP process is dark, and is costly to bleach.

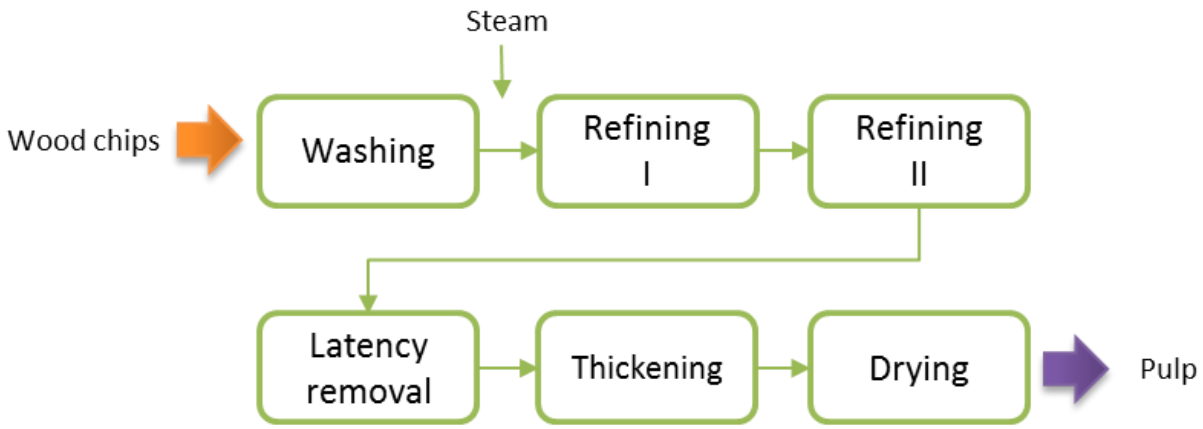


Figure 2-4 Basic flow diagram of the TMP process [15]

2.2.2.2 Kraft Pulping

Kraft pulping is the dominant pulping method in the world [17]. In the Kraft process, chips are cooked in a solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), then the wood fibres are separated from lignin by dissolution [15]. After delignification, the cellulose fibres are

separated from the spent liquor (black liquid) and bleached by adding chemicals. Finally the fibres are drained, pressed, and thermally dried. The removed black liquor is concentrated by evaporation and sent to the recovery boiler for steam production. A causticizer is used to regenerate the white liquor. A schematic of the Kraft process is shown in Figure 2-5.

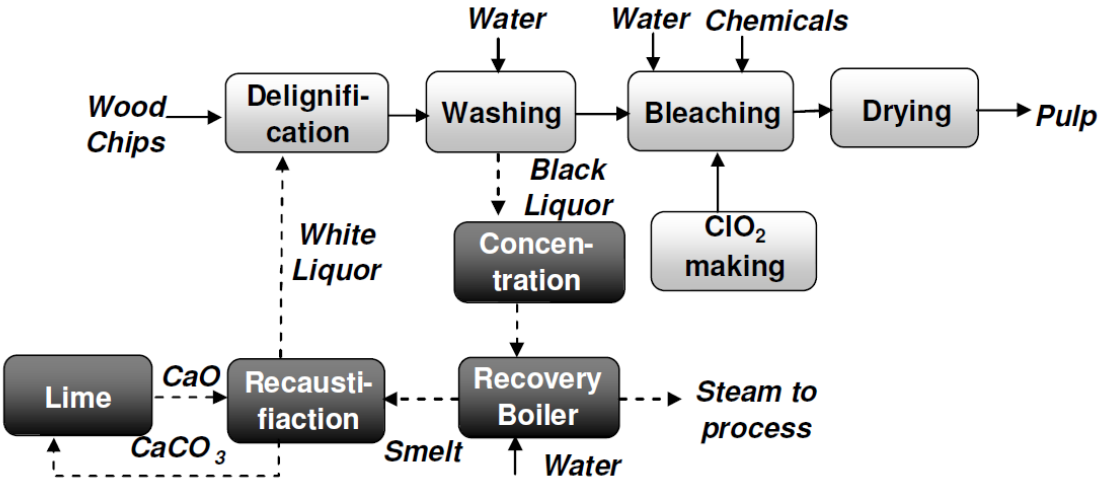


Figure 2-5 A simplified diagram of the Kraft process

2.2.3 Energy and water consumption in the pulp and paper industry

A large amount of water is consumed in the pulp and paper industry. It is used for the dilution of pulp, washing, cooling, and general cleaning operations. The larger the amount of water used and effluent produced, the larger the energy needed for heating, cooling and pumping the streams.

In 2005, 14% of the total water consumption in Canada was used in the manufacturing sector and 45% of the manufacturing share was supplied to the paper manufacturing [18]. The electricity consumption in the manufacturing areas of Canadian P&P mills is shown in Table 2-2.

Table 2-2 Energy consumption of pulp manufacturing areas [19]

Area	Electricity (kWh/ODT)	Thermal energy (GJ/ODT)
Wood Preparation	22.20	0
Kraft Pulping	169.30	4.94
Kraft Evaporators – Direct Contact	24.50	5.91
Kraft Recausticizing	32.10	0.14
Kraft Bleaching (Softwood / Hardwood)	179.50 / 143.90	3.41 / 2.33
Sulphite Pulping	766.40	5.00
Sulphite Acid Plant	32.00	N/A
TMP for Newsprint / Paper	2661.60 / 2943.20	0.56 / 0.67
SGW	1780.30	0

2.3 Biorefinery

According to the National Renewable Energy Laboratory of the US, a biorefinery is defined as a specific facility that converts biomass into various high-value products such as fuels, power, and chemicals. The biorefinery concept is analogous to the petroleum refineries that produce diverse fuels and products from petroleum. A comparison between the petroleum and the biomass-based refineries is shown in Figure 2-6.

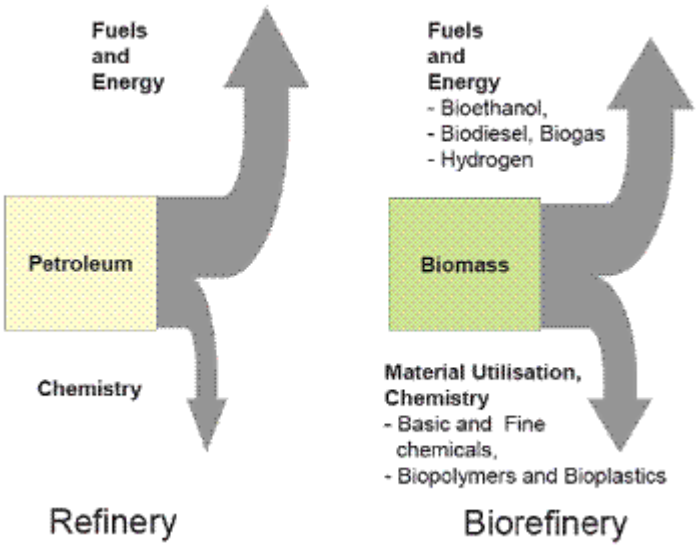


Figure 2-6 The petroleum refinery versus the biorefinery [20]

2.3.1 Biorefinery classification

The IEA has introduced a biorefinery classification system based on the complete biomass to end product chains: the raw material utilized, conversion processes, platforms, and final products generated [21].

- Various types of raw materials can be used in a biorefinery, including dedicated crops and residues. Depending on the raw material, biorefineries can be classified in 1st , 2nd, and 3rd generation [22]. As the first generation biorefinery uses starch based biomass (e.g. grain crops), it causes several side-effects such as a destabilization of the world grain price, a risk of depletion of minerals in soil, and a competitive use of arable land [23]. The second generation biorefinery uses 'plant biomass' refers largely to lignocellulosic biomass that are cheap, abundant, and non-food materials [24]. Using the 2nd generation biorefinery is recommended to prevent the issues of the 1st biorefinery, however, as these 2nd generation biorefinery is relatively immature, the products are not cost-effective. So they should have good potential for cost reductions and increase of production efficiency. The third generation uses microalgae. Because microalgae can produce 15-300 times more oil for biodiesel production and have a very short harvesting cycle compared with conventional crops, it is considered to be an alternative energy resource. Although microalgae biorefinery has many advantages and potential benefits, some challenges including the production cost

of microalgae, environmental impacts from the microalgae production and waste treatment [25].

- The technologies that are capable of being applied to convert biomass feedstock into valuable products can be classified into four processes: mechanical /physical (pressing, milling, and separation), biochemical (fermentation, enzymatic conversion), chemical (hydrolysis, pulping), and thermochemical (pyrolysis, gasification, combustion) [21].
- The platform is an intermediate between the raw material and the final products such as sugars (C5/C6), syngas, biogas, hydrogen, lignin, and pyrolysis liquid [2].
- The final product can be broadly grouped into two classes: energy products and material products [22]. Energy products include biofuels such as bioethanol, biodiesel, biogas, and bioenergy (bio-steam). Material products include chemicals and building blocks and polymers, for example, amino acids, xylitol, succinic-, lactic-, levulinic acid, furfural, PLA etc [2].

2.3.2 The integrated forest biorefinery (IFBR)

The integrated Forest Biorefinery (IFBR) is the integration of one or more bio-processing facilities that use lignocellulosic biomass into an existing process such as a pulp and paper mill in order to reduce costs of investment and operation by sharing infrastructure. Figure 2-7 represents an example of an integrated biorefinery based on the Kraft mill and the possible interactions.

Pulp and paper mills are appropriate sites for the integration of a biorefinery process, because they are located near to the raw material, and they have an extensive experience to handle biomass and utilities such as steam and water that can be transferred to the biorefinery.

The integration of a bio-process in a P&P mill can affect the quality of the pulp produced and the material and energy balance. For example, the integration of a lignin extraction technology to a P&P mill would affect its energy balance. The extraction of hemicelluloses from wood chips before pulping will impact both the material balance and the heating value of the black liquor.

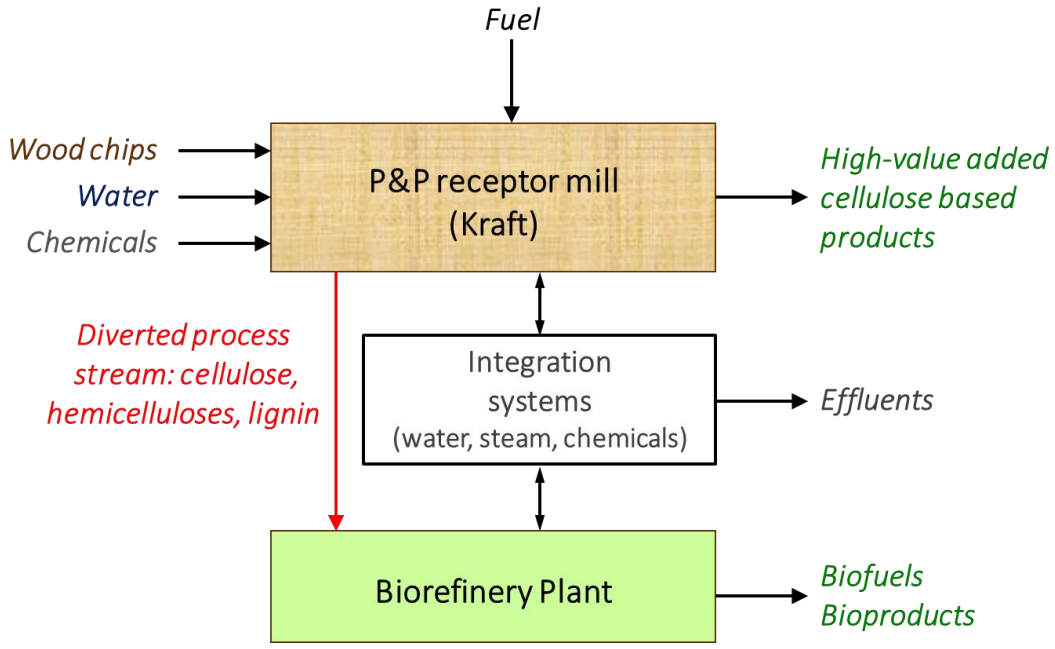


Figure 2-7 Distribution and share of resources in an integrated biorefinery complex

2.3.3 The sugar platform

Burning is the most basic way to use lignocellulosic biomass to produce heat and electricity. However, there is great potential in the use of lignocellulosic biomass to produce liquid fuel or chemicals. In order to make possible the use of lignocellulosic biomass as feedstock for the production of bio-based products, it is fundamental for them to be converted to a sugar platform [23].

Cellulose and hemicellulose are hydrolyzed using biochemical or chemical pathways to produce sugars that can be converted to various bio-chemical products including bio-ethanol/butanol or organic bio-acids (lactic, succinic, etc.), as shown in Figure 2-8. After the hydrolysis step, the stream contains not only sugars but also toxic compounds such as hydroxymethylfurfural (HMF), acetic acid, formic acid, and phenolic compounds, therefore, a detoxification step is essential to purify the stream and to use the sugars.

The production of bio-ethanol by the conversion of glucose via a biochemical pathway is well-developed process at the industrial scale. Yeasts are mainly used as micro-organisms during the fermentation because of their characteristics: high ethanol yield, tolerance to ethanol, toxicity, and high fermentation ability at a low pH [26]. However, yeasts cannot ferment xylose that is derived

from hemicelluloses. To overcome this limitation, researches on the genetic modification of yeasts are developing new microorganisms [27]. Finally a recovery step with distillation is used and a pure ethanol stream is obtained.

Above bio-ethanol, various building blocks can be produced from sugars by certain micro-organisms at appropriate temperature and pH conditions. In this perspective, detailed process configurations for the production of bio-based lactic and succinic acid from lignocellulosic biomass will be reviewed in Section 2.4.

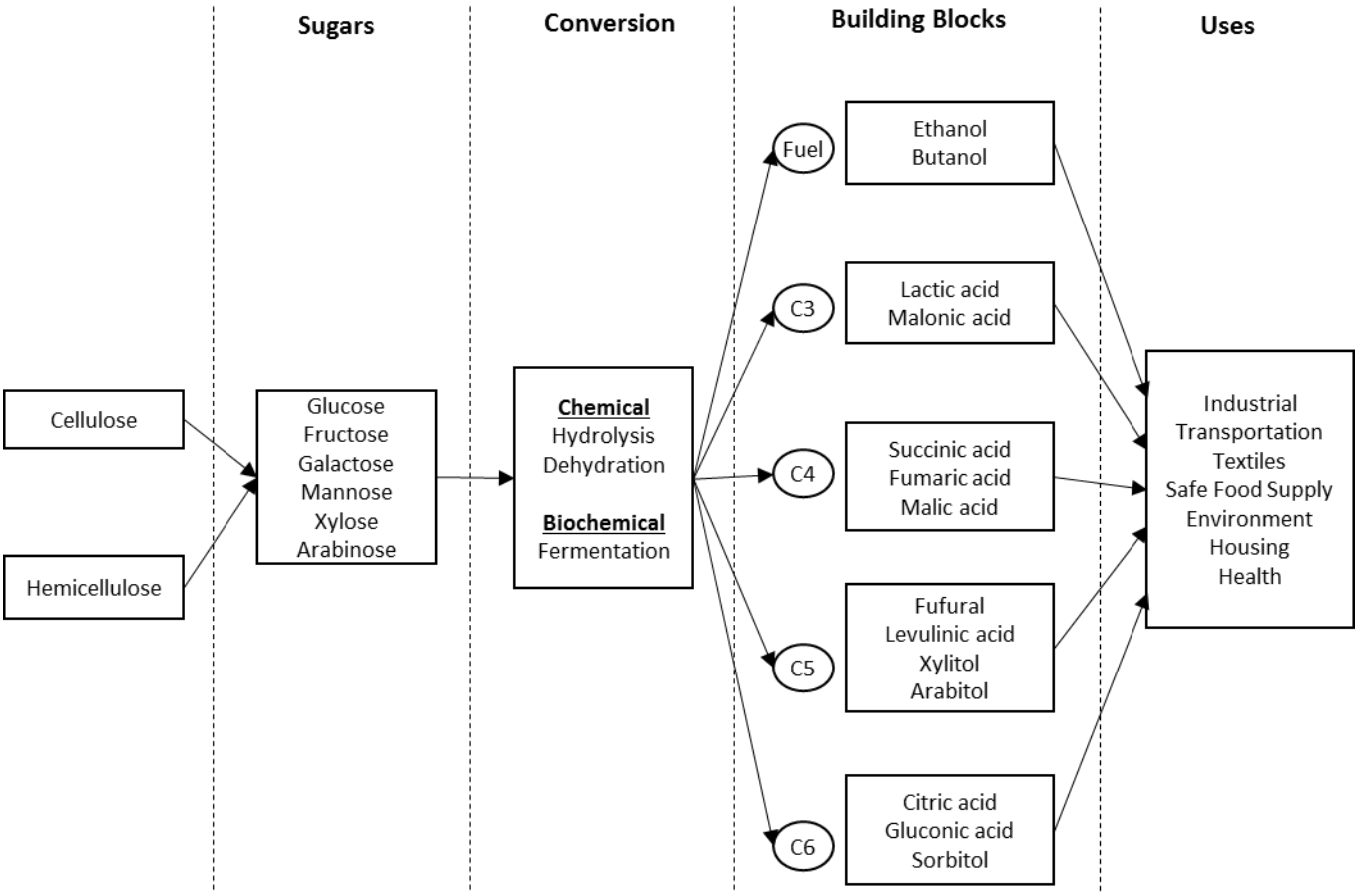


Figure 2-8 Bio-based products from cellulose and hemicelluloses

2.3.3.1 Lactic acid

Lactic acid ($C_3H_6O_3$) is an organic acid naturally occurring with a long history of use for fermentation in food. Lactic acid was discovered in sour milk and considered as a milk component

by Scheele in 1780. In 1857 Pasteur discovered that it is a fermentation product by certain microorganisms [28].

Lactic acid has various applications in the food, pharmaceutical, cosmetic, and chemical industries [29]. In recent years, there has been a growing interest in Poly Lactic Acid (or PLA) which is a biodegradable plastic synthesized from lactic acid [30]. As a feedstock of PLA, the global demand of lactic acid has been increasing rapidly. In 2013, the global lactic acid and PLA market was estimated to be 714.2 kilo tons and 360.8 kilo tons respectively, and is expected to reach 1,960 kilo tons and 1,205.3 kilo tons by 2020 [31].

Lactic acid can be manufactured by both chemical and biological pathways (Figure 2-9). The chemical synthesis needs petrochemical feedstock and produces a racemic mixture of D(-)-lactic acid and L(+)-lactic acid which is not suitable for the production of PLA; the biobased production uses carbon sources such as corn, lignocellulosic biomass, or cheese whey and creates optically pure lactic acid [32]. Therefore, the biological pathway of lactic acid production has received significant interest. Around 90% of the lactic acid at commercial scale is produced by the biological pathway.

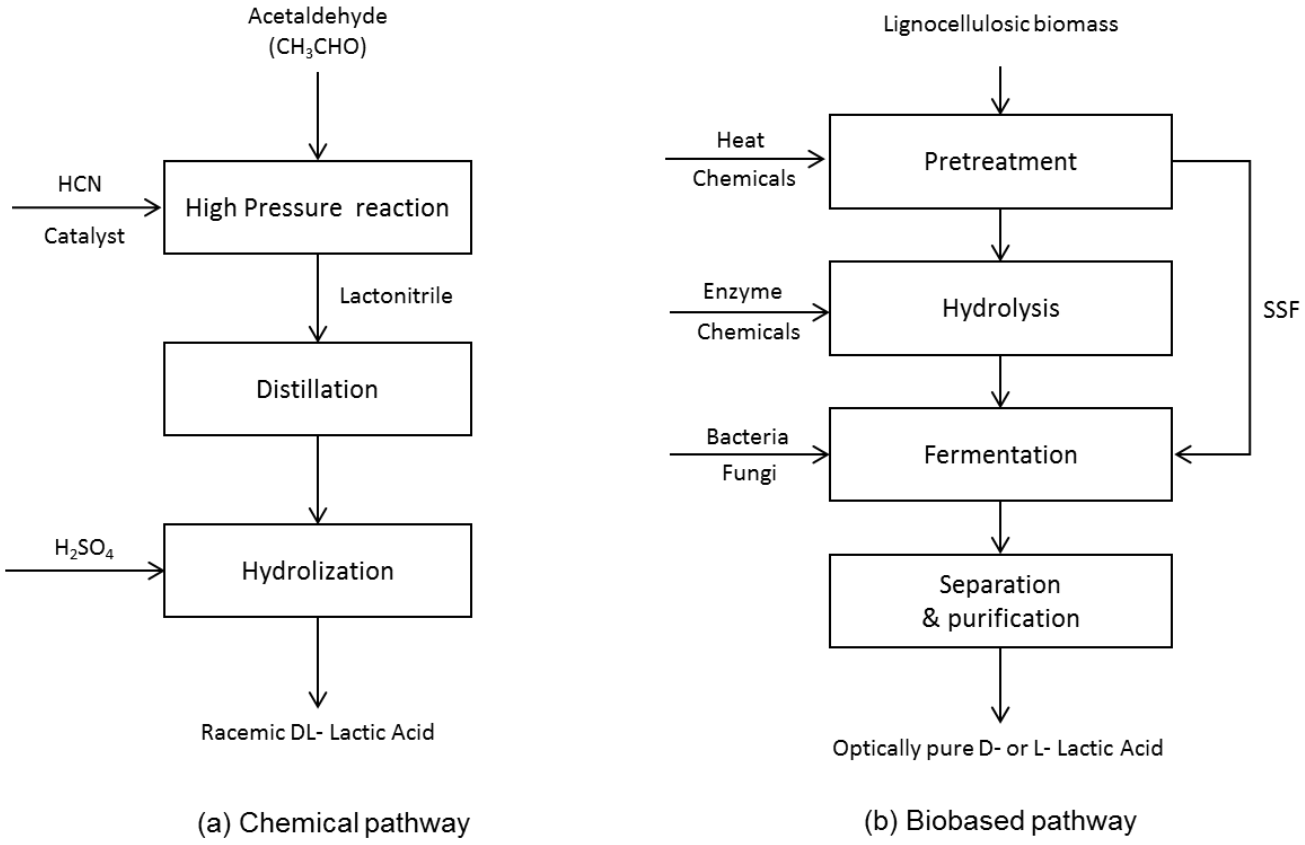


Figure 2-9 Overview of the two manufacturing methods for the production of lactic acid [33]

The major manufacturers of biobased lactic acid are NatureWorks (USA, 180,000 tons), Purac (Thailand, 100,000 tons), Henan Jindan (China, 100,000 tons). Among them, NatureWorks started the first commercial-scale plant of PLA that produces 140,000 tons per year [34].

2.3.3.2 Succinic acid

Succinic acid (or butanedioic acid, $C_4H_6O_4$) is a metabolite participating in the TCA (tricarboxylic acid) cycle and could be a final product of fermentation of various bacteria and fungi [35]. It is also known as an amber acid because it has originally been obtained from amber by distilling in 1550.

It is widely used as a precursor of many chemicals with applications in chemical, food, and pharmaceutical industries [36]. In addition, as the synthesis of biodegradable polymers (like polybutylene succinate, polyamides and various green solvents) has been expending in the recent years, the market is expected to increase [37].

Conventional succinic acid is produced from butane by the conversion of maleic anhydride, however the operation is complex, expensive and causes environmental contamination. Recently the production of succinic acid by the bio-based pathway using fermentation has increased.

The global succinic acid market was estimated to 40,000 tons in 2011 and is expected to reach about 600,000 tons in 2020 [38]. Currently, 97% of the succinic acid is produced via the petrochemical pathway and the main producers are Gadiv petrochemical Industries, Mitsubishi Chemical, Kawasaki Kasel Chemical, Nippon Shokubai, and several Chinese companies. The main producers of bio-based succinic acid are Succinity (25,000 tons/year, Spain), BioAmber (3,000 tons/year, France and 35,000 tons/year, Ontario), Myriant (5,000 ton/year, Germany), and Reverdia (10,000 tons/year, Italy) [38].

2.4 LA/SA Production from biomass

Bio-based lactic and succinic acid production from biomass feedstock is obtained through the fermentation of sugars by microorganisms. The pre-treatment and hydrolysis steps are necessary depending on the type of biomass. The configurations of the process for the production of lactic and succinic acids from lignocellulosic biomass consist of five steps: i) pretreatment, ii) enzymatic hydrolysis, iii) detoxification, iv) fermentation, and v) product recovery.

2.4.1 Pretreatment

Lignocellulosic feedstock (LCF) has a strong structure to protect itself from physical, chemical and biological attacks occuring in nature due to its inner complex linkages between cellulose, lignin, and hemicellulose. Therefore, the pretreatment process is a critical step in the biorefinery. The main goals of the pretreatment are removing lignin and changing the primary structure to make the reaction between cellulose, hemicellulose and enzymes (that converts carbohydrate polymers into mono sugars) more effective in the hydrolysis step [39]. The effect of pretreatment is illustrated in Figure 2-10.

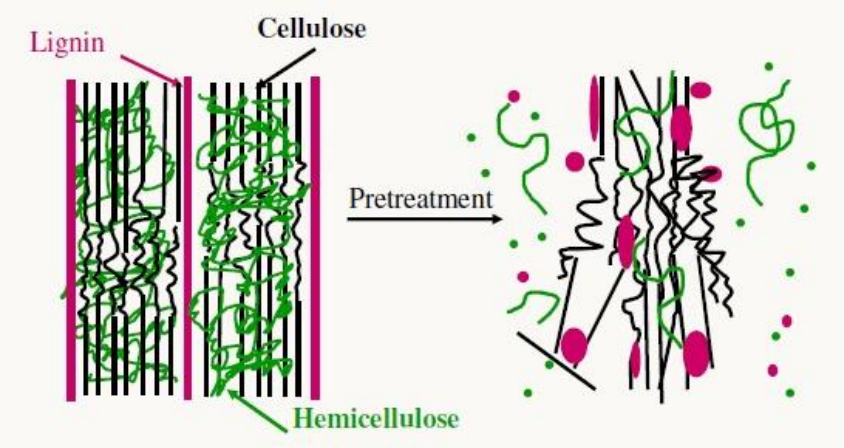


Figure 2-10 Modification of the lignocellulosic structure during pretreatment [40]

Given that each pretreatment process has advantages and disadvantages, it is important to choose an appropriate process according to the raw materials and the desired final products. Some features have to be considered: high recovery of carbohydrates, less inhibitors produced, less energy demands, less catalysts or chemicals added, and less capital costs. Table 2-3 shows the comparisons of the main pretreatment routes.

Table 2-3 Advantages and disadvantages of different pretreatment methods of linocellulosic biomass [41, 42]

Pretreatment	Advantages	Disadvantages
Mechanical	- Simple operation - Handle large volumes of biomass - No use of chemicals - Very little inhibitors generated	- Low sugar yield - High energy consumption - Requires an additional pretreatment step
Dilute acid	- Dissolution of hemicelluloses - High sugar yield	- High costs of acids and need for neutralization - Corrosive resistant equipment are required - Formation of inhibitors

AFEX	- Effective for agricultural biomass - High sugar yield - Low formation of inhibitors	- Recycling of ammonia is needed - Hemicelluloses are not hydrolyzed
Steam explosion	- No corrosion equipment required - Suitable for hardwood	- Formation of inhibitors - Requires washing of the treated biomass or conditioning of the hydrolyzate to remove inhibitors

2.4.2 Enzymatic hydrolysis

In the pretreatmnet step, the bonds of cellulose and hemicelluloses can be broken into oligosaccharides. These oligosaccharides should be broken to fermentable monosaccharides. Enzymatic hydrolysis is a very promising method to obtain fermentable sugars from pretreated lignocellulosic biomass. The main goals of the enzymatic hydrolysis are the break of chemical linkages in polysaccharides and the obtention of monosaccharides [43]. The enzymes are generally classified as cellulases and hemicellulases, suitable to convert cellulose and hemicellulose into sugars, respectively. Mixtures of theses enzymes are used to maximize the yield of hydrolysis and to decrease the reaction time and the process cost [44]. Enzymatic hydrolysis allows to produce relatively pure sugars, which can be done in mild operating conditions, without environmental and corrosion problems. However, a preliminary biomass pretreatment is required, the cost of enzymes is high, and the hydrolysis rate is low.

2.4.3 Detoxification

The pretreatment and hydrolysis steps may result in the production of inhibitors that are toxic for the fermentation microorganisms. The inhibitors can be classified in three groups: furan compounds (furfural and HMF) derived from sugars, weak acids (acetic, formic, and levulinic acid), and phenolic compounds due to the degradation of lignin [45]. As an example, the formation of acetic acid and furfural can prevent yeasts from growing and producing ethanol [46]. It is demonstrated that the phenolic components destroy and damage the cell membrane [47]. To correct

this, it is necessary to remove the inhibitors before the fermentation. The detoxification methods can be categorized in physical, chemical and biological, as shown in Table 2-4.

Table 2-4 Main detoxification methods for inhibitors removal

Methods		Features	Ref
Physical	Membrane (Nanofiltration or ultrafiltration)	High cost Selective removal of inhibitors	[48]
	Evaporation (Vacuum evaporation)	Reduce volatile compounds (acetic acid, furfural)	[49]
Chemical	Activated charcoal	Low cost Remove phenolics and furans Low sugar loss	[50]
	Ion Exchange Resin	Reduce phenolics Recycle is possible Difficult to scale-up	[51]
	Overlimming	Addition of $Ca(OH)_2$ High sugar loss	[48]
	Extractive solvents (liquid-liquid extraction)	Using ethyl acetate, trialkylamine Remove acetic acid, furfural, and phenolics High cost of operation Long process time	[52]
Biological	Enzymes	Little waste generated Environmentally friendly Long process time High cost of enzymes	[53]

2.4.4 Fermentation

2.4.4.1 Lactic acid fermentation

The production of bio-based lactic acid is based on the fermentation of sugars by several microorganisms such as bacteria, fungi, and yeast. Lactic Acid Bacteria (LAB), such as *lactobacillus*, *lactococcus*, and *E.coli* strains can produce lactic acid with high yield at pH condition of 5~7 and temperature of 35~45 ℃ [54].

LAB are classified into two groups according to the fermentation end product: homo-fermentative or hetero-fermentative (Table 2-5). The conversion reactions of the C6 and C5 sugars by homo-fermentative LAB can be described by the following equations [34, 55]:

- $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$
- $3C_5H_{10}O_5 \rightarrow 5C_3H_6O_3$

The theoretical yield of lactic acid production is 2 mol/mol glucose and 1.67 mol/mol xylose, on the other hand, the maximal yield of hetero-fermentative LAB is only 1 mol/mol sugar [34]. While the homo-fermentative LAB converts glucose into lactic acid almost exclusively, the hetero-fermentative LAB produces mixture of lactic acid, ethanol, CO_2 and acetic acid. The ratio of ethanol to acetic acid is dependent on the redox potential in the cells.

Table 2-5 Homofermentive and heterofermentative lactic acid bacteria [34]

	Homofermentative LAB	Heterofermentative LAB
Products	Lactic acid	Lactic acid, ethanol, formic acid, acetic acid, carbon dioxide
Theoretical yield of lactic acid from sugar	2.0 mol / mol glucose 1.67 mol / mol xylose	1.0 mol / mol glucose 1.0 mol / mol xylose
Strain	*Lactococcus, Enterococcus, Lactobaillus*	*Leuconostoc, Oenococcus*
Availability for commercial production	Available due to high yield	Not available due to high by-product formation

The high production yield and the safety make homofermentative LAB suitable for the production at the commercial scale. Most LAB strains used in the commercial production of lactic acid belong to *lactobacillus* because they are tolerant to acid and easy to be engineered for the selective production of lactic acid [56, 57].

Generally, LAB need complex nutrition including amino acids, peptides, and vitamins because of their limited ability to grow. This not only increases the production costs but also prevents the recovery of lactic acid. *E.coli* and yeast need simple nutrition that facilitates the recovery of lactic acid. Moreover, the tolerance of yeast to pH is as low as 1.5, which makes fermentation possible without the use of neutralizing agent. However, a wild type of *E.coli* produces a mixture of ethanol and several organic acids and a wild type of yeast hardly produces lactic acid.

The moderate temperature condition in LAB fermentation needs less energy but it increases the risk of contamination of the fermentation broth. In addition, the low fermentation temperature hinders the use of Simultaneous Saccharification and Fermentation (SSF) of lignocellulosic biomass that is carried out at higher temperature than that of LAB fermentation. Therefore, research on the use of genetically engineered yeast for the fermentation of lactic acid to compensate the difficulties related with nutrients and recovery is ongoing.

2.4.4.2 Succinic acid fermentation

Succinic acid can be produced via the fermentation of carbon sources by several microorganisms at 37~39 ℃, pH 6~7.5, in presence of CO_2. The overall yield can vary depending on the supply of CO_2 and hydrogen:

- $C_6H_{12}O_6 + CO_2 \rightarrow C_4H_6O_4 + CH_3COOH + HCOOH$ [58]
- $7C_6H_{12}O + 6CO_2 \rightarrow 12C_4H_6O_4 + 6H_2O$ [59]
- $C_6H_{12}O_6 + 2CO_2 + 2H_2 \rightarrow 2C_4H_6O_4 + 2H_2O$ [60]

The supply of CO_2 is an important factor for the fermentation of succinic acid. At low CO_2 availability, the formation of microorganism and succinic acid is strongly inhibited [61]. Both external CO_2 gas and carbonates in the medium resulting from the addition of $CaCO_3$, $NaCO_3$, or $MgCO_3$ can be a source of CO_2.

In addition to CO_2, H_2 is considered as a potential electron donor that affects the cellular metabolism. For a ratio of 5 % H_2 / 95% CO_2, the succinic acid production yield is increased by 5.86% compared with 100% CO_2 [62].

Actinobacillus succinogenes isolated from rumen is reported to produce a large amount of succinic acid from various carbon sources such as glucose, arabinose, xylose, galactose, mannose, sorbitol, cellobiose [63]. *Acinobacillus succinogenes* tolerates high concentrations of glucose, which is advantageous for fermentation [37]. Theoretically, 1 mol of CO_2 is spent to produce 1 mol of succinic acid. *Actinobacillus succinogenes* 130Z is an appropriate candidate that can be used to produce large amounts of succinic acid. The variant strain produces succinic acid up to 85% yield (g SA/ g glucose) and concentration of 68.5 g/L [64].

Anaerobiospirillum succiniciproducens isolated from the throat of dogs can produce succinic acid from renewable sources such as whey or wood hydrolysate [65, 66]. An important issue with this strain is the synchronous fermentation of the mixture of C5 and C6 sugars. It is reported that *A. succiniciproducens* produces succinic acid with 91.8% yield (g SA/ g glucose) and concentration of 30.5 g/L [67].

Another promising succinic acid bacteria, *Manheimia succiniciproducens,* is isolated from the bovine rumen and is also a capnophilic bacterium which grows well in presence of CO_2. It is expected to be able to produce 1.71 mol of succinic acid from 1 mol of glucose if the supply of CO_2 is enough [37].

Likewise with lactic acid bacteria, succinic acid producers require complex nutrition, including nitrogen sources and mineral salt for their metabolism and a strict pH control in the medium is essential. Therefore, there are vigorous research works on the use of genetically modified *E.coli*, *Corynebacterium glutamicum*, or yeast which needs simple nutrient to make the recovery step easier.

2.4.5 Separation and Purification

2.4.5.1 Lactic acid recovery

In the fermentation broth, lactic acid exists as a form of lactate salt rather than free lactic acid because of the neutralizing agents ($CaCO_3$, $Ca(OH)_2$, NaOH, and NH_3) that were added to control

the pH at 5~7 in the fermenter. The purification of lactic acid is one of the major steps that affects the global production cost and the final quality of lactic acid at commercial scale production.

Precipitation (Figure 2-11) is widely used as a traditional separation method. The fermentation broth is first neutralized by calcium carbonate so that a pH of 10 is reached and then heated at the temperature of 80 ℃. The high temperature and pH let the remaining proteins coagulate and make the filtration simpler [68]. The liquor is then filtered to remove cells, evaporated and acidified by adding sulfuric acid to turn lactate salt into lactic acid and $CaSO_4$ in the precipitation step [69]. The insoluble $CaSO_4$ is removed by filtration. Esterification, distillation and hydrolysis are finally performed to get pure lactic acid [70].

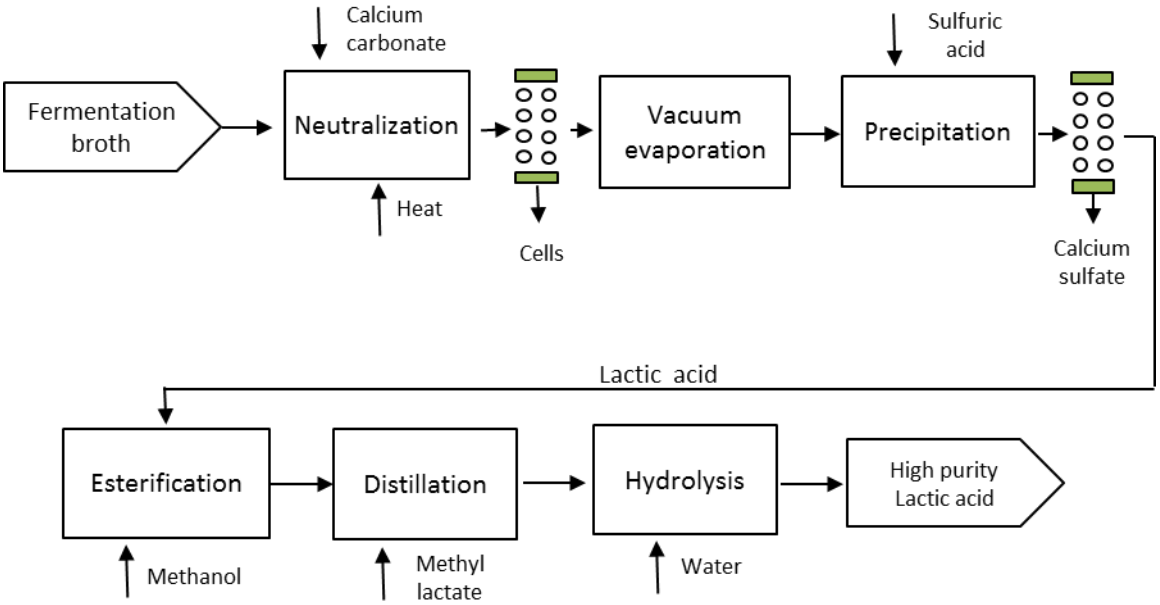


Figure 2-11 Conventional method (precipitation) for LA purification and final separation

The conventional process can be described by the following reactions:

– Neutralization:

$$2C_3H_6O_3 + CaCO_3 \rightarrow (C_3H_5O_3)_2Ca + H_2O + CO_2$$

– Precipitation by H_2SO_4:

$$(C_3H_5O_3)_2Ca + H_2SO4 \rightarrow 2(C_3H_6O_3) + CaSO_4$$

- Esterification:

$$C_3H_6O_3 + CH_3OH \rightarrow C_4H_8O_3 + H_2O$$

- Hydrolysis by H_2O:

$$C_4H_8O_3 + H_2O \rightarrow C_3H_6O_3 + CH_3OH$$

The disadvantages of this method are the generation of gypsum as a by-product and the high cost of the chemicals consumed.

There are several alternatives to the conventional separation such as electrodialysis, adsorption, reverse osmosis, reactive extraction, and liquid membrane [71]. These separation methods are more expensive but environment-friendly and energy-saving compared to the conventional process [72].

Among these methods, the electrodialysis is considered to be a potentially attractive process because it is a sustainable technique, which makes possible to treat quickly and obtain high concentrations of lactic acid [73]. In addition, an in-situ recovery system makes the relief of the product inhibition, which may cause the reduction of pH in the fermenter.

Electrodialysis is a process that is performed to separate ions from the fermentation broth under the influence of a direct current. The basic principle is that positively (cations) or negatively (anions) charged ions migrate toward the cathode or the anode, respectively (Figure 2-12). In desalting electrodialysis, ion-exchange membranes that can transfer cations or anions selectively are used. Because cations (sodium or ammonium ions) move across the cation exchange membranes in the direction to the cathode but they cannot pass the anion exchange membranes, so cations reach the compartment. On the other hand, anions (lactate ions) go through the anion exchange membranes towards the anode [74]. Finally, the originally-fed solution becomes diluted while the solution in the adjacent compartment is concentrated. Therefore, highly-concentrated lactate salt can be obtained from the fermentation broth.

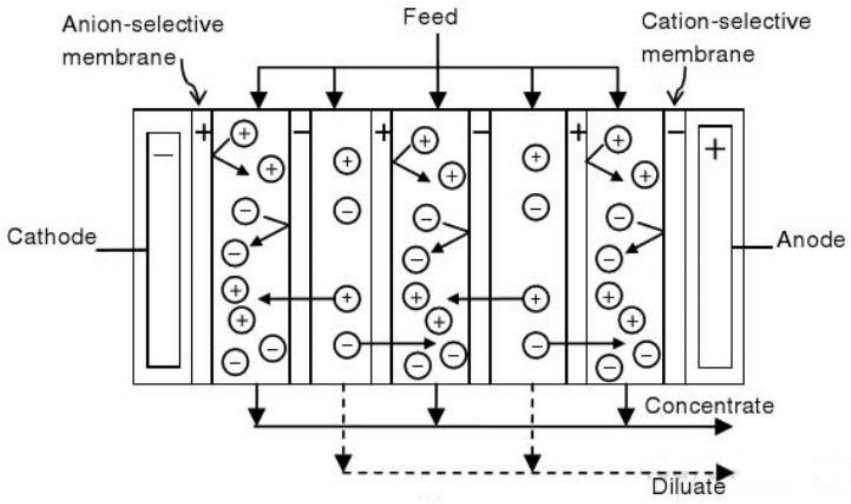


Figure 2-12 Principle of the conventional electodialysis

Desalting electrodialysis is used first to concentrate lactate and bipolar membrane electrodialysis is then applied to turn lactate into lactic acid by acidification [75]. After the desalting eletrodialysis, water-splitting electrodialysis (Figure 2-13) with the bipolar membrane is done to produce lactic acid from lactate salt and the resulting base is recycled to the fermentation step as a pH controller [76]. Bipolar membranes can separate water to H+ and OH- ions and convert ionic salt into acids and bases without chemical addition. To obtain pure lactic acid, further purification by ion exchange is required [75].

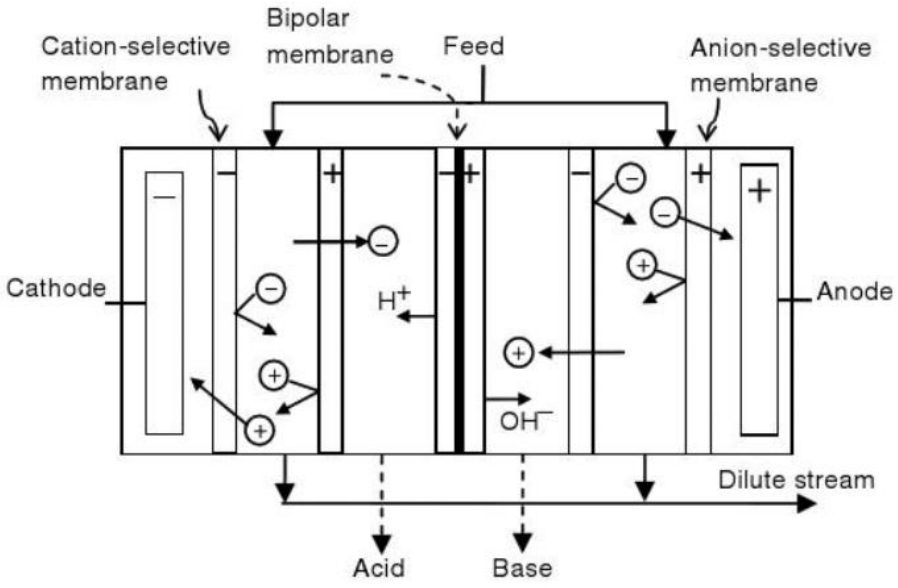


Figure 2-13 Water-splitting electrodialysis (with bipolar membranes)

Recently, various techniques of eletrodialysis for lactic acid recovery have been studied. The application of one-stage water splitting electrodialysis, combined nanofiltration and watersplitting electrodialysis has been reported [77]. Another particular process was proposed as well that is combined with desalting electrodialysis, water-splitting electrodialysis, esterification, and distillation, called the 'double ED' process, (Figure 2-14) has been developed at the Michigan Biotechnology Institute (MBI) [70]. However, there is still a challenge involved in a co-instantaneous operation of the fermentation and the electrodialysis.

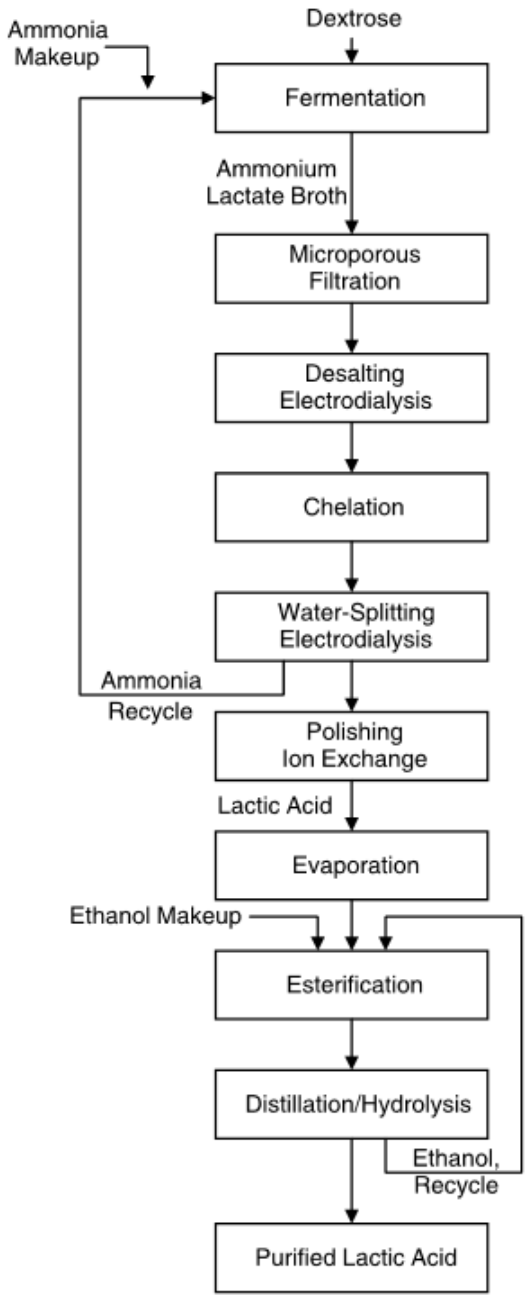


Figure 2-14 Double-ED process schematic [70]

2.4.5.2 Succinic acid recovery

The purification and downstream processing represent a large part of the total cost of biobased succinic acid production. The purification consists of two processes: the removal of the cells and the rest of the nutrients, and the conversion of succinic salts to succinic acid. Because of the neutral agents added in the fermentor to adjust the pH value around 7 for the growth of microorganism, the resulting products exist in a form of succinic salts in the broth.

$Ca(OH)_2$ is usually added to neutralize the fermentation broth and to precipitate calcium succinate at the same time. Calcium succinate is separated by filtration and converted to succinic acid by adding sulfuric acid [78]. However, a large amount of by-product calcium sulfate ($CaSO_4$) is generated and an important amount of the chemicals which cannot be regenerated are consumed with this method.

Reactive extraction with amine-based extractants has also been reported in many studies in the literature because of its easy operation at mild temperature and pressure conditions [79].

Vacuum distillation combined with crystallization was developed, which enables the removal of by-products such as acetic, formic acids from the broth and crystalizes succinic acid [80].

Electrodialysis (Figure 2-15) is used to separate succinate from non-ionized compounds such as carbohydrates, proteins and amino acids, then water-splitting electrodialysis converts succinate salt to succinic acid [81].

Recently, the application of one-step recovery method which crystallizes succinic acid directly in the fermentation broth was reported [82]. In the neutral solution, about 90 % of the succinic acid and by-products such as formic, lactic and acetic acid exist in their ionic forms. When the pH value of the solution is 2.0, the solubility of succinic acid is only 3%. On the other hand, the by-products still have larger solubility in the fermentation broth at pH 1.0~1.4 and temperature of 0~4 ℃. Therefore, succinic acid can be selectively separated by crystallization if the pH is controlled at 2.0 by adding HCl. According to the report of Qiang et al., 70% yield and 90% purity of succinic acid using this process can be obtained [82].

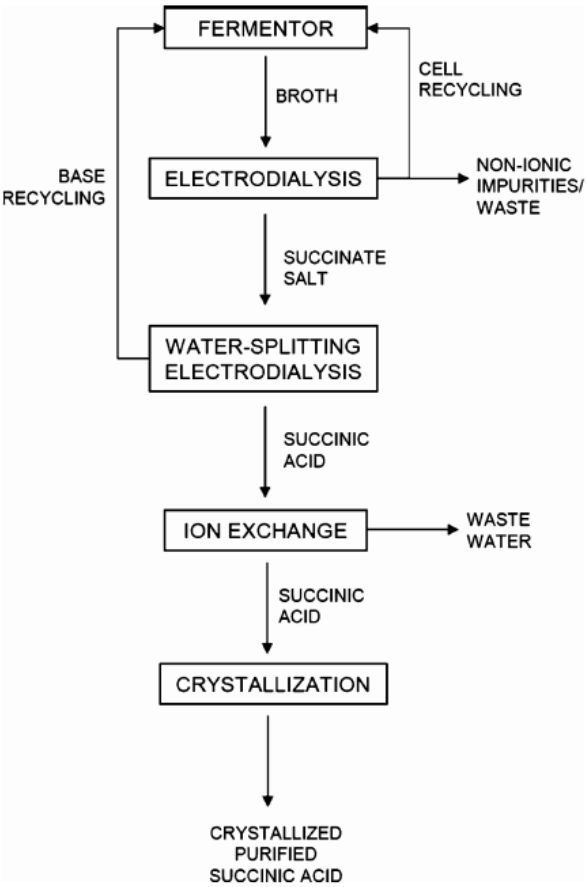


Figure 2-15 Process combining electrodialysis and water-splitting electrodialysis [83]

2.5 Process integration and internal heat recovery

When a biorefinery process is added to an existing pulp and paper facility, it is unavoidable that the demands for heating and cooling increase. However, building a new utility system, including a cooling tower and a steam boiler in a stand-alone design is not cost-effective. Therefore, it is imperative to analyze the process and to identify opportunities for heat integration and energy reduction in order to decrease the energy demand and the operation costs. Pinch Analysis can be applied to the heat integration studies.

2.5.1 Pinch Analysis

The Pinch Analysis, which was developed by Linnhoff et al. in 1982, is a widely-used method for energy integration [84]. It provides a systematic methodology to save energy within a process by maximizing internal heat recovery and minimizing external hot and cold energy demands supplied

by utilities. It also provides systematic guidelines to design a heat exchanger network for the maximum internal heat recovery and optimal utility use.

In order to start a pinch analysis, thermal data such as in/out temperature and heat load of streams are extracted from the process. The streams are identified as either hot, which need to be cooled, or cold, which need to be heated. The total energy excess or deficit can be illustrated separately by means of the Composite Curves where enthalpy is represented on the x-axis against temperature on the y-axis (Figure 2-16 a). Once the construction of the hot and cold composite curves is done, the cold composite curve is moved toward the hot composite curve in order to obtain the minimum energy target (Figure 2-16 (a)). The minimum temperature difference, ΔT_{min}, determines the closest point between the curves and the minimum temperature difference in a heat exchanger. The Composite Curves provide several important features of the thermal system, such as (Figure 2-16(b)):

- Maximum potential heat recovery, Q_{Rmax}: the overlap between the composite curves.
- Minimum hot utility requirement, Q_{Hmin}: the remaining heating needs.
- Minimum cold utility requirement, Q_{Cmin}: the remaining cooling needs.

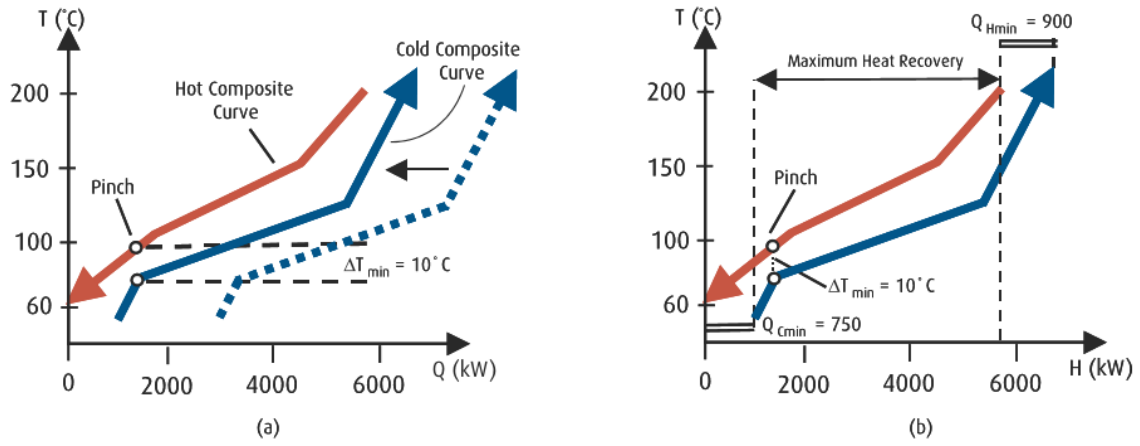


Figure 2-16 Building and use of the composite curves to determine the energy targets [85]

The point of closest approach between the hot and the cold composite curves is called “Pinch point”. It separates the system into two regions: one above the pinch is the heat sink and one below

the pinch is the heat source. In Pinch Analysis, three rules should be followed to reach the minimum energy targets of the process:

- Heat must not be transferred across the pinch
- No external cooling above the pinch
- No external heating below the pinch

For the selection of ΔT_{min}, the consideration of a trade-off between capital and energy costs is required. Higher value of ΔT_{min} causes higher hot and cold utility requirements while lower ΔT_{min} needs larger and more expensive heat exchangers in P&P processes. The optimum ΔT_{min} is approximately 10~20℃ [86].

The composite curves provide the overall energy targets. However, they do not show how much energy must be supplied based on the utility conditions. The energy can be supplied by various utility levels such as different steam pressure levels, cold water, refrigeration, etc. It is necessary to design heat exchangers that maximize cheaper utility levels and minimize expensive utility levels in order to save energy cost. In fact, it is encouraged to use LP steam or cooling water instead of HP steam or refrigeration because of their cost. Therefore, the grand composite curve is used to choose the appropriate utility levels and to target the optimal heat loads.

To build the Grand Composite Curve, hot and cold composite curves are shifted by moving down the hot curve and moving up the cold curve, each by ½ ΔT_{min} until they touch at the pinch point (Figure 2-17 (b)). The grand composite curve is drawn by plotting the heat load difference between the hot and the cold composite curves, as a function of the temperature (Figure 2-17 (c)). The pinch point is where the curve touches the y-axis. From the Grand Composite Curve, the utility levels required for the process can be chosen.

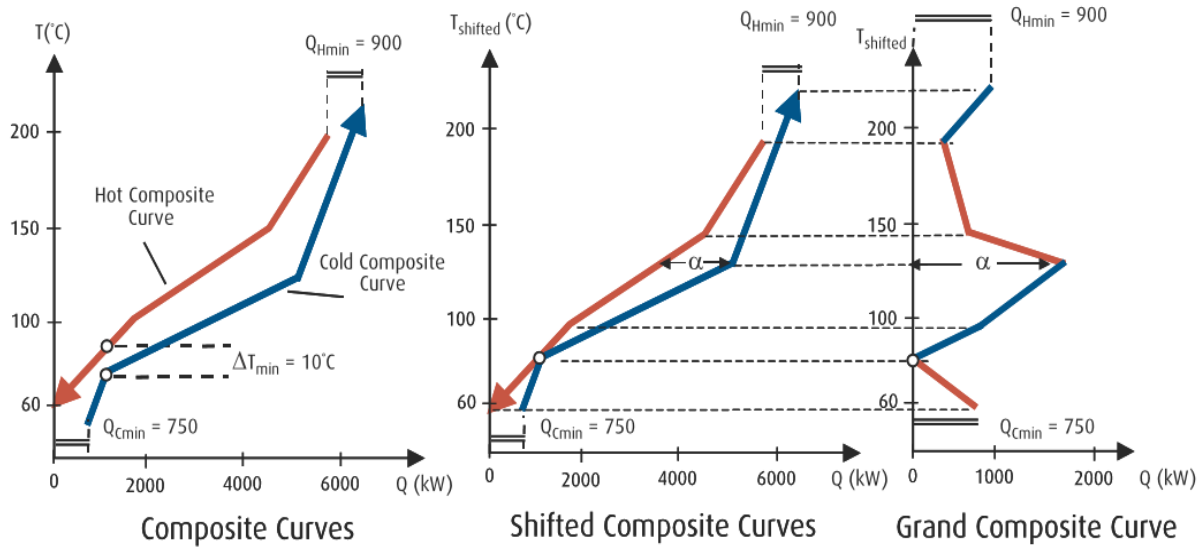


Figure 2-17 Construction of the grand composite curve [85]

2.6 Water pinch

Over the past two decades, there has been a growing concern regarding freshwater consumption and wastewater treatment in the industry. The purpose of water pinch analysis is to reduce flows going to the water treatment process and to reuse them where possible. Its principles are similar to those of thermal pinch analysis. However, the driving force is the difference of contaminant concentration. Similarly in the way as energy pinch does, water purity profiles that correspond to composite curves in energy pinch are built. The flow rate is indicated on the horizontal axis and water purity is represented on the vertical axis. By moving both water source and sink curves until they touch at the pinch, water purity profiles are completed. The water pinch indicates the amount

of water that can be re-used (overlapped parts), the minimum wastewater generated (on the left), and the minimum freshwater consumed (on the right) (Figure 2-18).

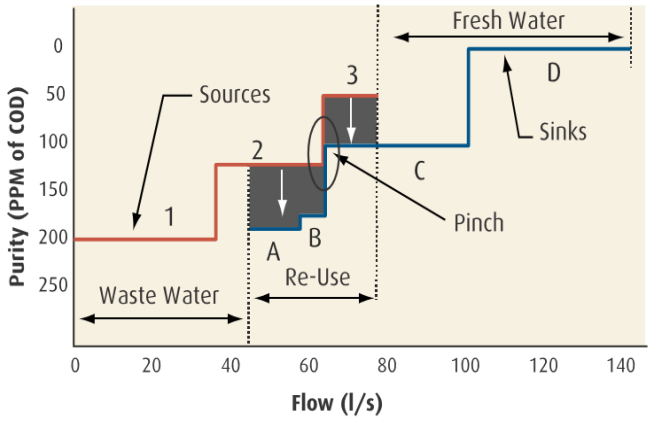


Figure 2-18 Water purity profiles [85]

2.7 Energy and water pinch analysis in P&P mills

pinch analysis is applied in many energy-intensive industries such as oil refining, pulp and paper, or textiles to reduce external fossil fuel consumption [86]. In the old pulp and paper mills, pinch analysis has not be considered for the energy recovery. Therefore, it is possible to obtain economically attractive energy savings just by respecting the pinch rules [87]. Actually, the Augusta Newsprint Company in the US identified overall steam savings of 42% and cost savings of $7.15 per ton of paper, Kimberly Clarke's Coosa Pines facility in US achieved energy savings of 22% and cost savings of $15.4 per ton of paper [88]. Lafourcade, S. et al. carried out pinch analysis on TMP mills and improved the energy efficiency: the steam consumption has dropped from 60.5 ton/h to 56.1 ton/h [89]. Jacob et al. proposed water network optimization methods that can be applied to pulp and paper mills [90]. Mateos et al. performed an interaction study between the water and energy systems in a Kraft mill, showing synergistic effects of water reutilization on energy consumption [91, 92].

2.8 Critical review

Integrated forest biorefinery (IFBR) has been recommended as a reasonable alternative to overcome the current operational risk of the P&P mills and to find sustainable fuels and chemicals that can substitute petroleum-based process. The interaction between the biorefinery and the existing pulp mill in terms of material and energy should be considered without negative impacts on the quality of final products.

So far, several studies for the development of an IFBR concept were performed. However, many researches have dealt with specific parts of the process configuration in biorefinery such as pretreatment, hemicellulose extraction technology, or combining of black liquid gasification instead of the overall process [79, 93, 94].

In addition, most of the studies are focused on the Kraft pulp mill as a biorefinery receptor mill [95]. There are 28 mechanical pulp mills and 24 Kraft pulp mills in Canada [19], and the economic value of their manufacturing in 2010 were 973 M$ and 5 659 M$, respectively [96]. Therefore, research work on IFBR with a mechanical pulp mill as a receptor mill is also needed.

Most of studies on the IFBR consider the production of bio-ethanol [97], however, it is important to expand the types of final products to various value-added chemicals to diversify the sources of revenue.

In this work, overall process configurations for the production of bio-based lactic and succinic acid from a hydrolysate diverted from a TMP process were developed and simulated on Aspen Plus. The interactions between the biorefinery plant and the TMP process were analyzed in terms of heat integration. Finally, the strategies and the technical/economic feasibility of a IFBR composed of a TMP mill and a LA/SA plant were discussed.

CHAPTER 3 OBJECTIVES AND METHODOLOGY

3.1 Objectives

The main objective of this study is to demonstrate the technical and economic feasibility of an integrated forest biorefinery (IFBR) composed of a TMP process and a biorefinery plant for the production of lactic or succinic acid.

The specific objectives of this work are to:

- Review the production processes for lactic and succinic acid.
- Propose process configurations for the production of lactic and succinic acid from forest biomass.
- Develop simulation models for both lactic and succinic acid on ASPEN Plus.
- Perform energy analysis by using Pinch Analysis.
- Evaluate the proposed process configurations to identify the effects from energy perspectives (e.g. heat integration potential, minimum hot and cold utility demand).
- Demonstrate the technical and the economic feasibility of the concept of integrated forest biorefinery (IFBR) in a TMP process.

3.2 Methodology

The methodology used to develop the lactic and succinic acids IFBR is illustrated in Figure 3-1. The project consists of five phases that are listed below:

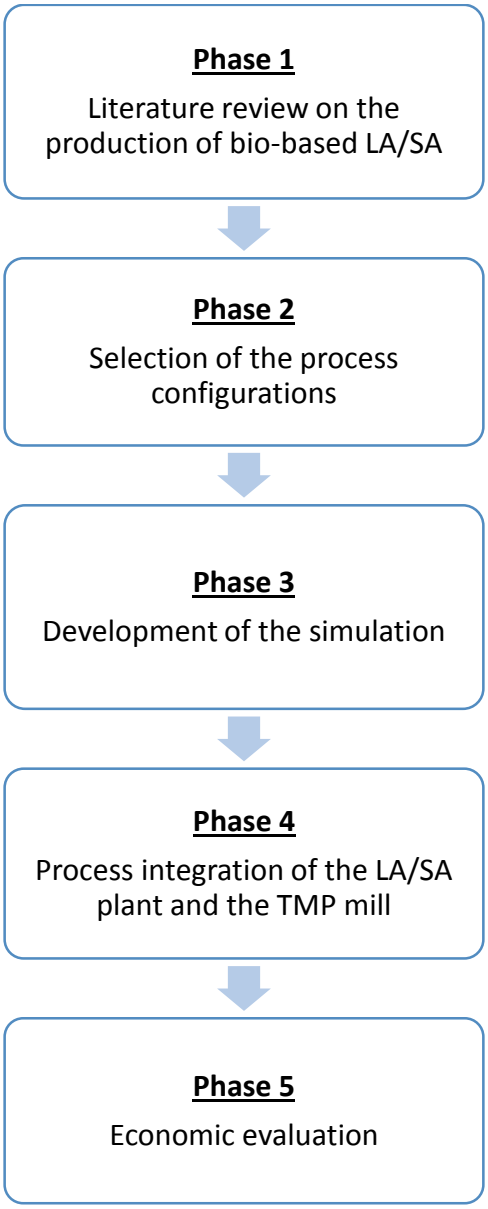


Figure 3-1 Overview of the methodology for the bio-based lactic and succinic acids IFBR development

Phase 1 – Literature review for the production of bio-based lactic and succinic acids:

In the first phase, a literature review on different configurations of biorefinery depending on raw material, final products, and recovery methods was conducted.

Phase 2 – Selection of the process configuration:

Two configurations for each final products (LA/SA) to be integrated to a TMP plant were selected. In addition, specific conditions such as temperature, pressure were selected in this phase. These conditions are used as input data in the simulation module.

Phase 3 – Development of the simulation:

The selected bio-refinery configurations for both lactic and succinic acid production, which represent four different processes, were simulated on Aspen Plus. The composition and the amount of feedstock were provided from FPInnovations. The material and energy balances were calculated in this phase.

Phase 4 – Process integration:

In the fourth phase, the process integration of the four stand-alone bio-based lactic and succinic acid plants into a TMP process was performed based on Pinch Analysis. The streams data of the TMP mill were provided by FPInnovations and those for the lactic and succinic acid plants were extracted from the Aspen Plus simulation. The energy target and the required utility levels of each stand-alone process were determined by the Composite Curve and the Grand Composite Curves. Aspen Energy Analyzer and Microsoft Excel were used in this phase.

During the process integration two scenarios were developed. In the first scenario, part of the streams of the stand-alone biorefinery plant that need hot utility (steam) were selected, and then the heat integration was performed with these streams and the TMP mill. In the second scenario, the heat integration was performed using all the streams of the stand-alone biorefinery plant and the TMP process. The impact of the integration and the heat recovery opportunities were evaluated and the Heat Exchange Network was designed.

Phase 5 – Economic evaluation:

Finally, an economic evaluation was performed. The economic viability of the IFBR between a LA or SA plant and a TMP mill has been assessed by calculating the payback period.

CHAPTER 4 DESIGN OF BIOREFINERY CONFIGURATIONS & SIMULATION DEVELOPMENT

4.1 Selection of the process configurations

The detailed explanation of the configurations selected in this study for the production of bio-based lactic and succinic acid from biomass was given in Section 2.4. In summary, there are five main steps for the production of lactic and succinic acid from lignocellulosic biomass by bio-based pathways: i) pretreatmnet, ii) enzymatic hydrolysis, iii) detoxification, iv) fermentation, and v) product recovery. Figure 4-1 illustrates the process configuration for the production of lactic and succinic acid from lignocellulosic and starch biomass feedstocks.

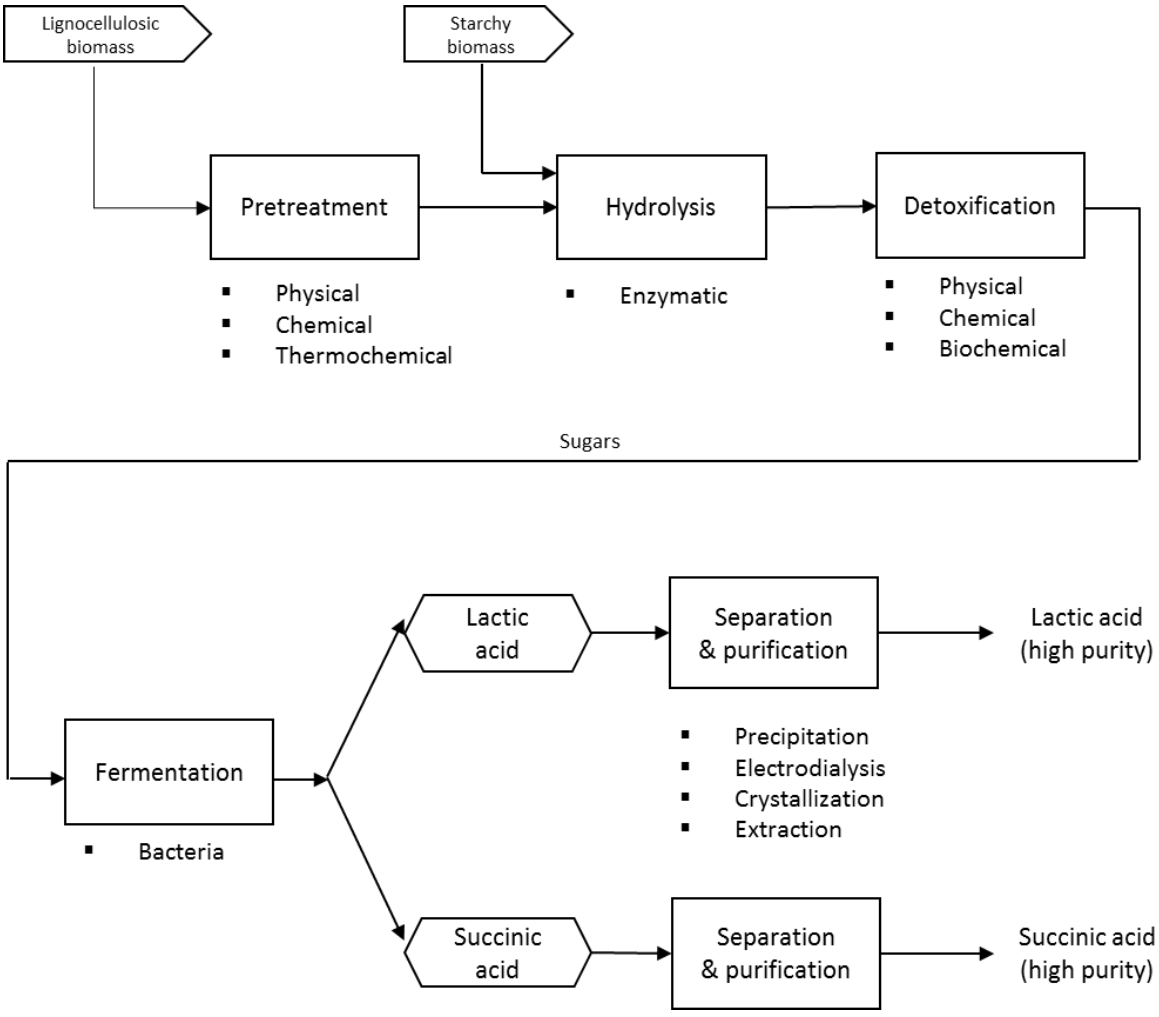


Figure 4-1 Configuration of the bio-based LA/SA production

In order to develop a simulation model, two configurations for both lactic and succinic acid were selected depending on the recovery method. The selection criteria are the high yield/purity of the final product, low energy consumption, availability in a commercial scale, and environmental sustainability (Table 4-1).

Table 4-1 The criteria used for process configurations selection

Process	Yield	Energy use	Commercial application	Environmental sustainability
LA production with the recovery by conventional method (precipitation)	√	√	√	
LA production with the recovery by electrodialysis	√			√
SA production with the recovery by direct crystallization	√	√	√	
SA production with the recovery by electrodialysis	√			√

Finally lactic acid production with the recovery by conventional method (precipitation) and electrodialysis, and succinic acid production with the recovery by direct crystallization and electrodialysis were chosen. In this project, as the feedstock is a pretreated sugar-rich stream diverted from a TMP process and the hydrolysate are almost pure sugars with very small amount of acetic acid, the pretreatment and the detoxification steps are not considered in the simulation. The final four configurations to be simulated and evaluated for the integrated forest biorefinery (IFBR) are presented in Figure 4-2.

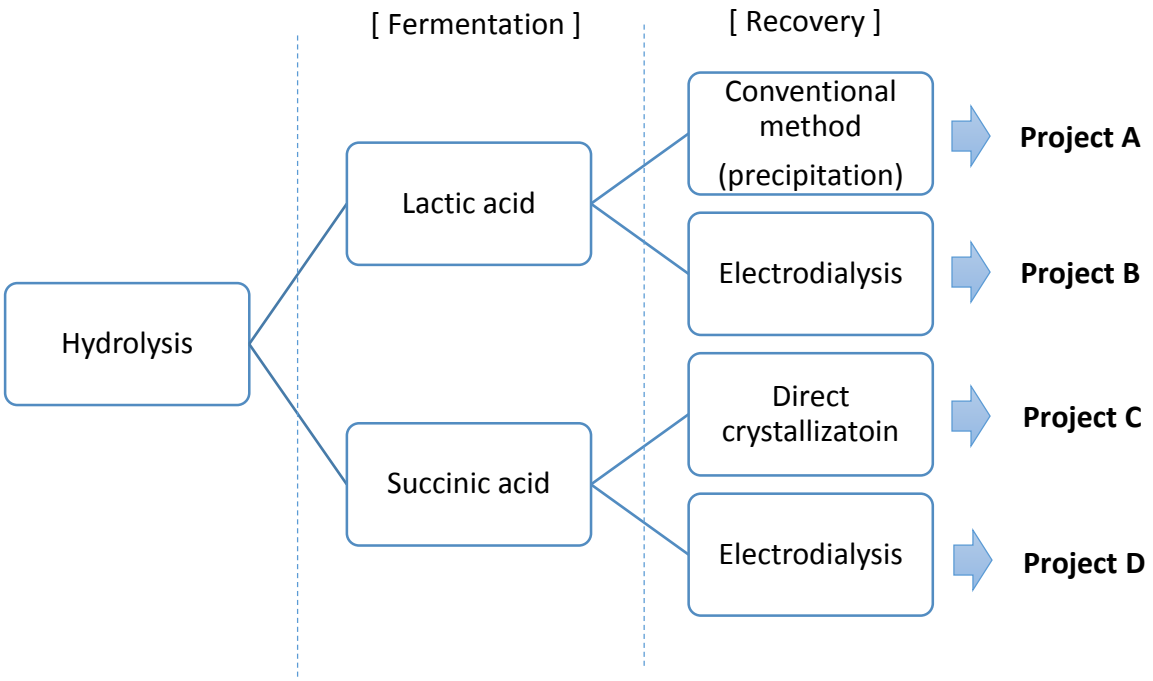


Figure 4-2 Configurations considered for the simulation

4.2 Development of the simulation models

To support the work, simulation models in Aspen Plus for stand-alone plants that produce bio-based lactic and succinic acid from lignocellulosic feedstock have been developed. The feedstock used and the hydrolysis step are the same for the four simulations. However, different reactions are applied for the production of lactic and succinic acid in the fermentation step. During the recovery process, the conventional method (Project A) and electrodialysis (Project B) are used for the purification of lactic acid, and the method of direct crystallization (Projcet C) and electrodialysis (Project D) are adopted for the succinic acid recovery.

4.2.1 Feedstock composition

In this project, the feedstock is a prehydrolysate of aspen wood chip submitted to a mild chemical treatment and a low pressure mechanical refining. The composition of the feedstock is supplied by FPInnovations [98]. Table 4-2 gives the composition of the feedstock and its representation in the Aspen Plus simulation. The amount of the feedstock was assumed to be 500 ton/day (dry basis).

Table 4-2 Representation of the feedstock composition in Aspen Plus [98]

Wood component	**Aspen Plus**	**%**
Glucan	CELLULOS	54.71
Xylan	XYLAN	14.37
Lignin	LIGNIN	23.1
Other Carbons	GALACTAN	2.91
Extractives	ASH	0.35
Unknown	ACETATE	4.56
Total		**100.00**

Some of the materials that do not exist in the conventional databank of Aspen Plus, but are involved in the production of lactic and succinic acid, such as cellulose, xylan, lignin, galactan, and ash, are taken from the NREL database [55]. The glucan is assumed to have the same properties as cellulose and the other carbons, extractives, and unknown components are considered as galactan, ash, acetate, respectively.

4.2.2 Enzymatic hydrolysis

In the hydrolysate supplied by FPInnovations, the pretreated stream is mixed with water and enzyme formulations from Novozymes. The properties of enzymes are assumed to be the same as those of zymo in the NREL data bank [55]. In Aspen Plus, the hydrolysis step is modeled as a stoichiometric reactor (RStoic). The remaining solid part and the enzymes in the resulting stream are separated by centrifugation. Figure 4-3 shows the flowsheet of the simulation of the enzymatic hydrolysis. The reactions that are assumed to occur in the enzymatic hydrolysis reactor are presented in Table A1 in Appendix A.

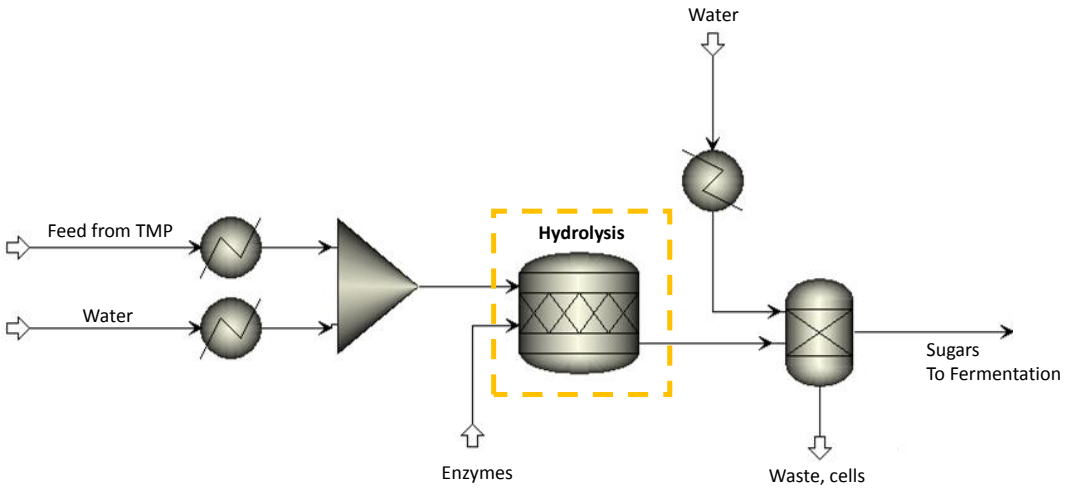


Figure 4-3 Flowsheet of the enzymatic hydrolysis step modeled in Aspen Plus

4.2.3 Lactic acid production

4.2.3.1 Lactic acid fermentation

For the simulation of the lactic acid fermentation, a stoichiometric reactor (RStoic) is used and the operating conditions (temperature of 49°C, pH of 5.8 to 6.0) are chosen based on the literature review [68]. The used microorganism is assumed to be *lactobacillus* (added 4g/L [99]) whose properties are supposed to be the same as those of biomass in the NREL data bank. Regarding the pH control, two different bases are added in the fermentation step depending on the method of separation. $Ca(OH)_2$ (49% [g/g sugar] [100]) is used for the separation by precipitation (conventional) and NaOH (160g/L [99]) is added for the separation by electrodialysis. The nutrient for the metabolism of the microorganisms is assumed to be a corn steep liquor (20 g/L [99]), the properties of which are taken from the NREL data bank. The reactions that are assumed to occur in the fermentation reactor are presented in Table A2 in Appendix A.

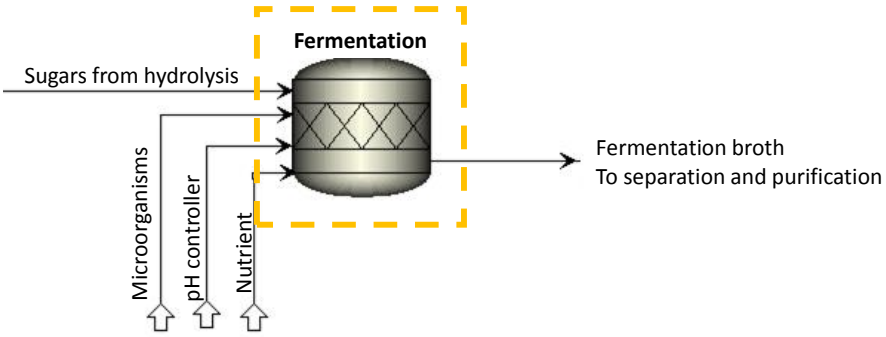


Figure 4-4 Flowsheet of the lactic acid fermentation

4.2.3.2 Lactic acid recovery

4.2.3.2.1 Lactic acid recovery by conventional method

The fermentation broth is filtered to remove cells, then heated to 70℃ to kill the bacteria and make the proteins coagulate. Stoichiometric reactor (RStoic) is used to simulate the precipitation step by adding sulfuric acid. Calcium lactate is converted to lactic acid by reacting with sulfuric acid. Gypsum is created as a by-product and is removed by filtration. The resulting lactic acid is sent to evaporation (100 ℃) to increase the concentration of lactic acid.

A further purification process is carried out by esterification, distillation and hydrolysis. A stoichiometric reactor (RStoic) is used for the esterification at 100 ℃, 1 atm, and methanol is added. During the esterification, lactic acid reacts with methanol and creates methyl lactate and vapor. The non-reacted methanol, methyl lactate and vapor are sent to first distillation unit, and the methyl lactate is separated in the distillation bottom. The distillation is simulated with the RadFrac model in Aspen Plus. The liquid phase of methyl lactate is converted to lactic acid and methanol in the hydrolysis reactor, which is simulated with RStoic. In the second distillation unit, the methanol is separated in the column head, then recycled to the esterification step and the lactic acid is sent to the distillation bottom. The simulation flowsheet of the lactic acid recovery steps with the conventional method is illustrated in Figure 4-5. The reactions that are assumed to occur are shown in Table A3 in Appendix A.

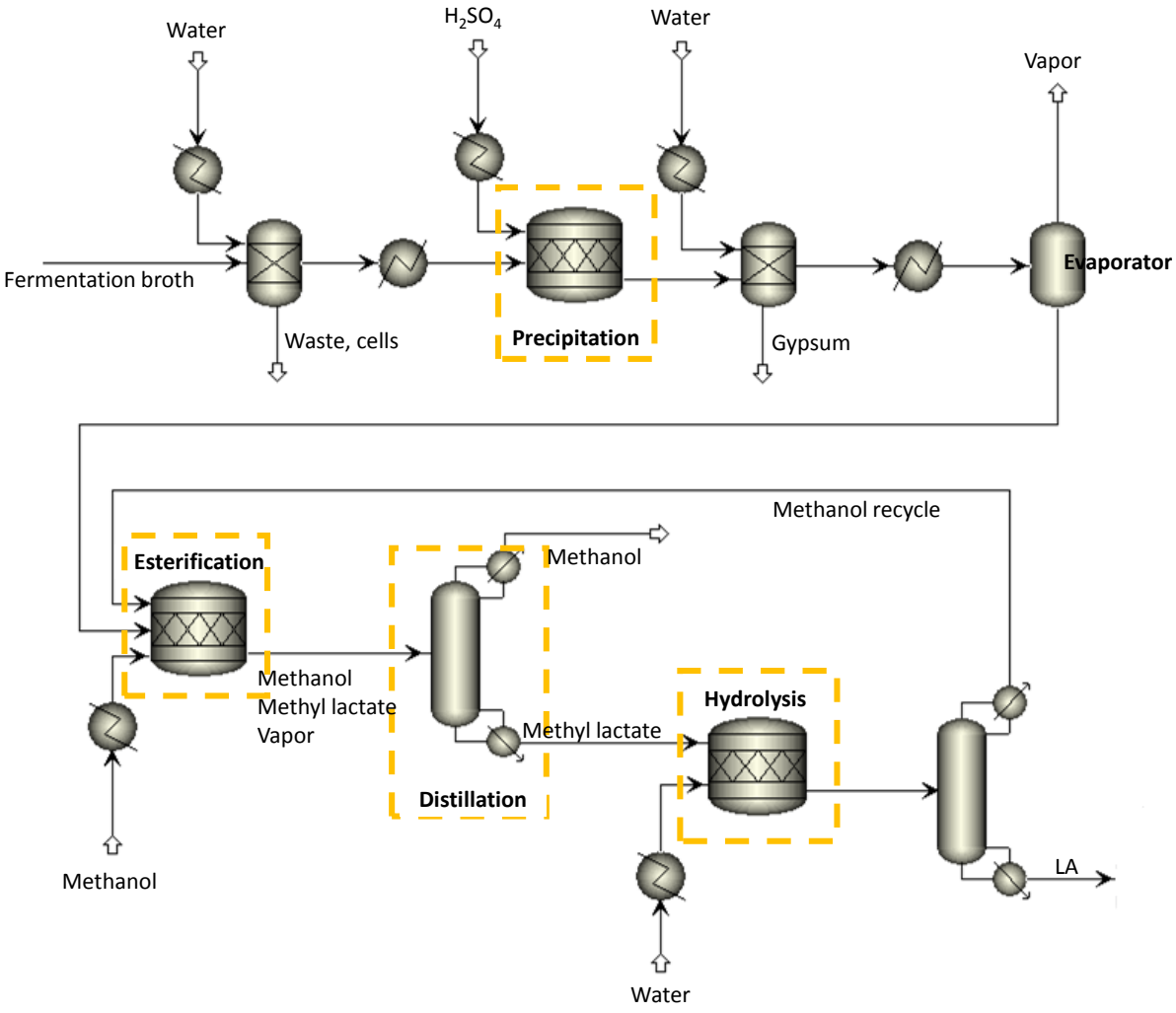


Figure 4-5 Flowsheet of the lactic acid recovery by conventional method (Project A)

4.2.3.2.2 Lactic acid recovery by electrodialysis

The fermentation broth is filtered to remove cells and the lactic acid is separated by electrodialysis. A separator is used to represent the electrodialysis step in Aspen Plus, the simulation flowsheet of the lactic acid recovery steps with electrodialysis is illustrated in Figure 4-6. After the electrodialysis, the remaining purification steps are the same as in Section 4.2.3.2.1.

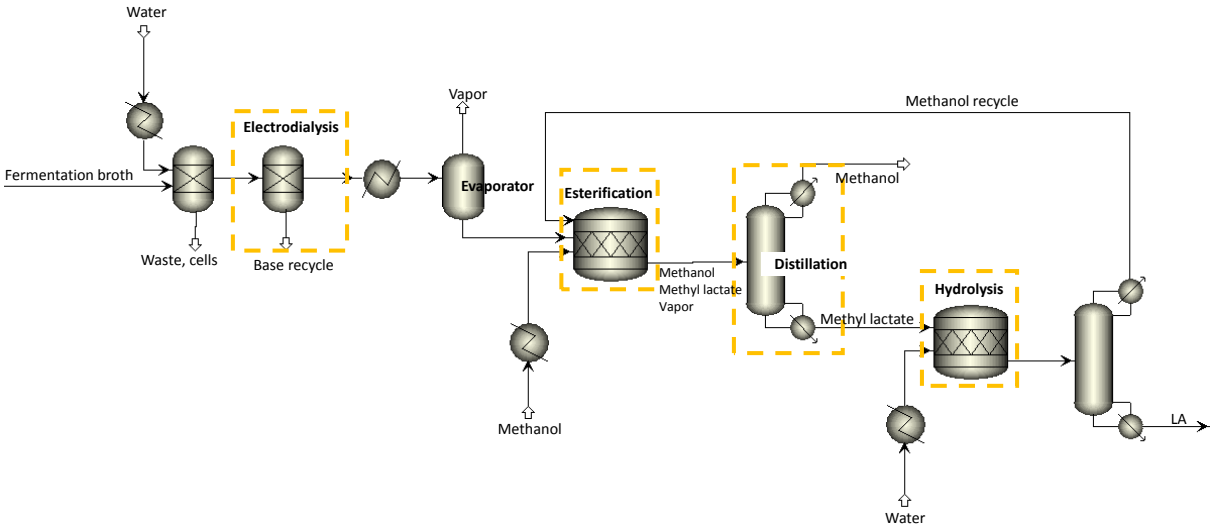


Figure 4-6 Flowsheet of the lactic acid recovery by electrodialysis (Project B)

4.2.4 Succinic acid production

4.2.4.1 Succinic acid fermentation

The operation conditions of the fermentation step are obtained from US patent (37℃, *aerobiospirillum succiniciproducens* strain) [64]. As in the lactic acid fermentation, a stoichiometric reactor (RStoic) is used and the properties of microorganism (added 2.5 g/L [101]) are supposed to be the same as biomass in Aspen Plus. NaOH is added (10 mol/L [102]) to control pH. The corn steep liquor (added 5 g/L [101]) is assumed as a nutrient for the metabolism of microorganism; the properties are taken from the NREL data bank. The simulation flowsheet of the succinic acid fermentation is illustrated in Figure 4-7.

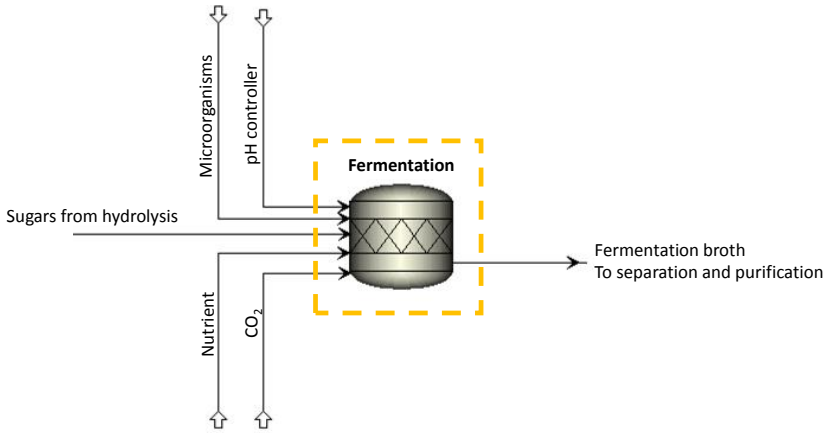


Figure 4-7 Flowsheet of the succinic acid fermentation

4.2.4.2 Succinic acid recovery

4.2.4.2.1 Succinic acid recovery by direct crystallization

The fermentation broth is filtered to remove cells, then sent to an evaporator (Flash2) operated at 102℃ and 1 atm [103]. Since the acetate and formate produced as by-products have a lower boiling points than succinate, they can be vaporised along with most of the water. At the bottom part of the evaporator, a concentrated succinate stream is obtained with a small amount of impurities. In the crystallization, HCl is added to lower the pH of the liquid to acidic conditions (pH 2), then cooled down to 4℃ where the solubility of the succinic acid is 3%. Only succinic acid is crystallized because acetic or formic acid impurities entering in the crystallisation vessel are considered soluble in water. The crystallized succinic acid is then dried. The simulation flowsheet of the succinic acid recovery by direct crystallization is illustrated in Figure 4-8.

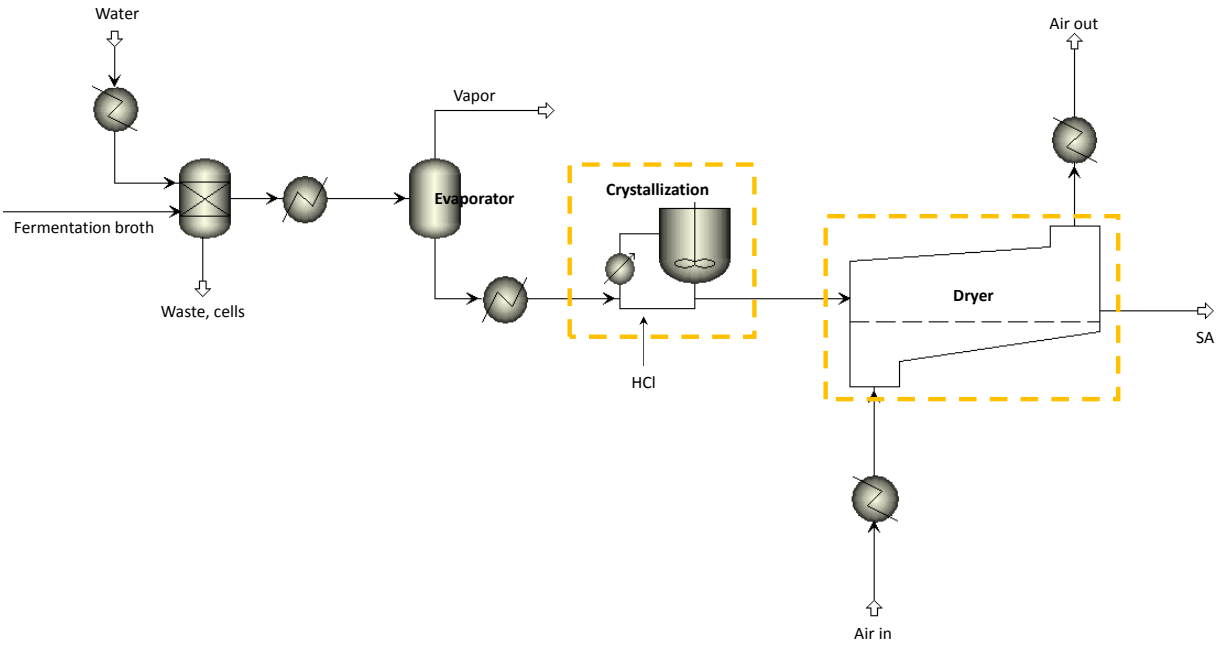


Figure 4-8 Flowsheet of the succinic acid recovery by direct crystallization (Project C)

4.2.4.2.2 Succinic acid recovery by electodialysis

The fermentation broth is filtered to remove the cells and the solution is treated by electrodialysis. A separator is used to represent the electrodialysis step converting succinate to succinic acid. The solution is concentrated by evaporation, crystallized, and dried. The specification of the

evaporation, the crystallization and the drying steps are the same as in 4.2.4.2.1. The simulation flowsheet of the lactic acid recovery steps using electrodialysis is illustrated in Figure 4-9.

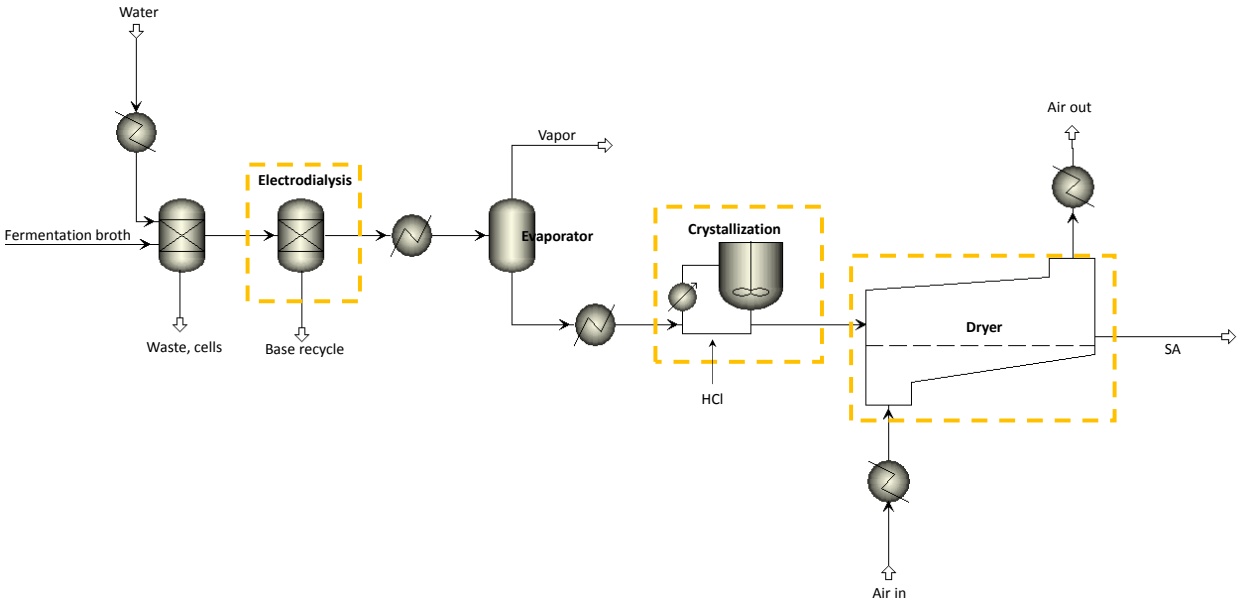


Figure 4-9 Flowsheet of the succinic acid recovery by electrodialysis (Project D)

4.3 Simulation results

Four different configurations were simulated using Aspen Plus: the production of lactic acid with the recovery by conventional method (precipitation, Project A) and electrodialysis (Project B), and the production of succinic acid with the recovery by direct crystallization (Project C) and electordialysis (Project D).

4.3.1 Stand-alone bio-based lactic acid production (Project A, B)

Figure 4-10 shows the results of the material balance obtained from the Aspen Plus simulation of the stand-alone bio-based lactic acid production using the conventional method for the final product recovery (Project A).

A stream of 500 ton/day (a pretreated stream diverted from the TMP mill whose components were given in Table 4-2 in Section 4.2.1) was sent to the enzymatic hydrolysis step and 240 ton/day of sugars were produced. In Table 4-3, the components concentration in the hydrolysates was calculated from the simulation results and was close to the FPInnovations data [98]. The results

generated from the enzymatic hydrolysis step will be also applied to the simulation of the succinic acid production in Section 4.3.2.

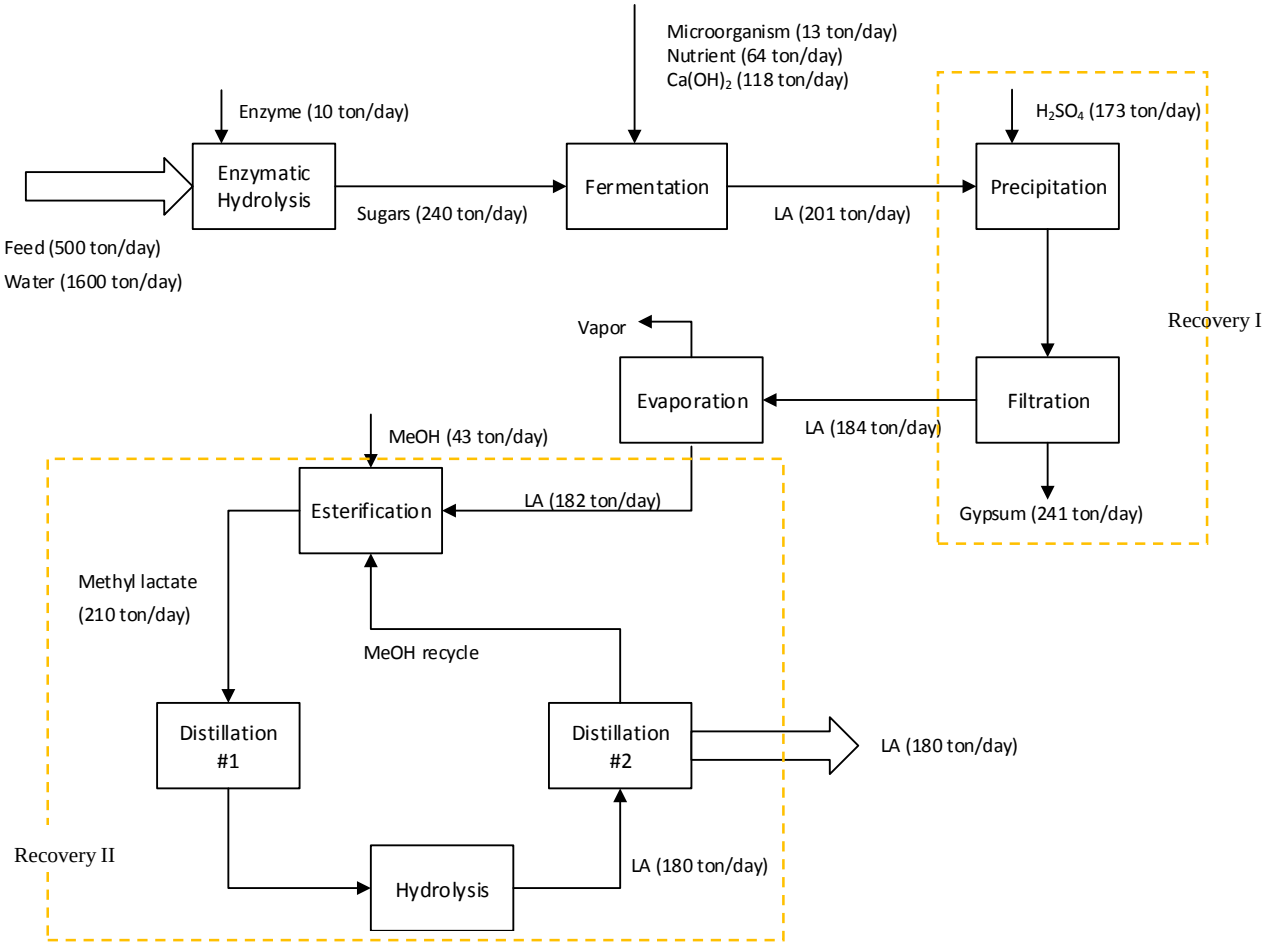


Figure 4-10 Material balance for the stand-alone bio-based lactic acid production with the recovery by conventional method (Project A)

Table 4-3 Concentration of components in the hydrolysate based on simulation results [g/L]

Composition	Concentration [g/L]
Glucose	92.2
Xylose	28.9
Oligosaccharides	10.9
Acetic acid	3.2

Microorganisms (Lactic Acid Bacteria) metabolize sugars (glucose, xylose) and produce lactic acid as a major metabolite during the fermentation at a temperature of 45 °C, pH of 7. During the fermentation, 201 tons of lactic acid were produced and 84% (g LA/ g sugar) yield was obtained.

In Figure 4-10, for the recovery by precipitation, after treatment with sulfuric acid, 241 ton/day of gypsum (calcium sulfate) were produced and 184 ton/day of lactic acid were recovered from the fermentation broth, with a 92% yield. After the further purification steps, 180 ton/day of lactic acid was produced, and overall 36% yield was obtained (g LA/g feedstock). Table 4-4 presents the most energy demanding steps of the process in the stand-alone bio-based lactic acid production using the conventional method in the recovery (Project A).

Table 4-4 The most energy demanding units in the lactic acid production with the recovery by the conventional method (Project A)

Unit	MW
Distillation #1	117.8
Distillation #2	59.0
Evaporation	84.3
Esterification	4.5
Hydrolysis	5.7

The material balance based on the Aspen Plus simulation of the stand-alone bio-based lactic acid production with the recovery by electrodialysis (Project B) is presented in Figure 4-11. The enzymatic hydrolysis and the fermentation step were the same as in the simulation of the Project A. As shown in Figure 4-11, the lactic acid recovered by electrodialysis from the fermentation broth was 190 ton/day, with a 95 % yield, then the stream is evaporated. Since electrodialysis requires electric energy, the electricity consumption in the electrodialysis (7MW) was included in the operating costs in the economic evaluation. After esterification, distillation, and hydrolysis, 184 ton/day of lactic acid was produced. An overall 36% yield (g LA / g feedstock) for the lactic acid production was obtained. Table 4-5 presents the most energy demanding process steps in the stand-alone bio-based lactic acid production with the recovery by electrodialysis (Project B).

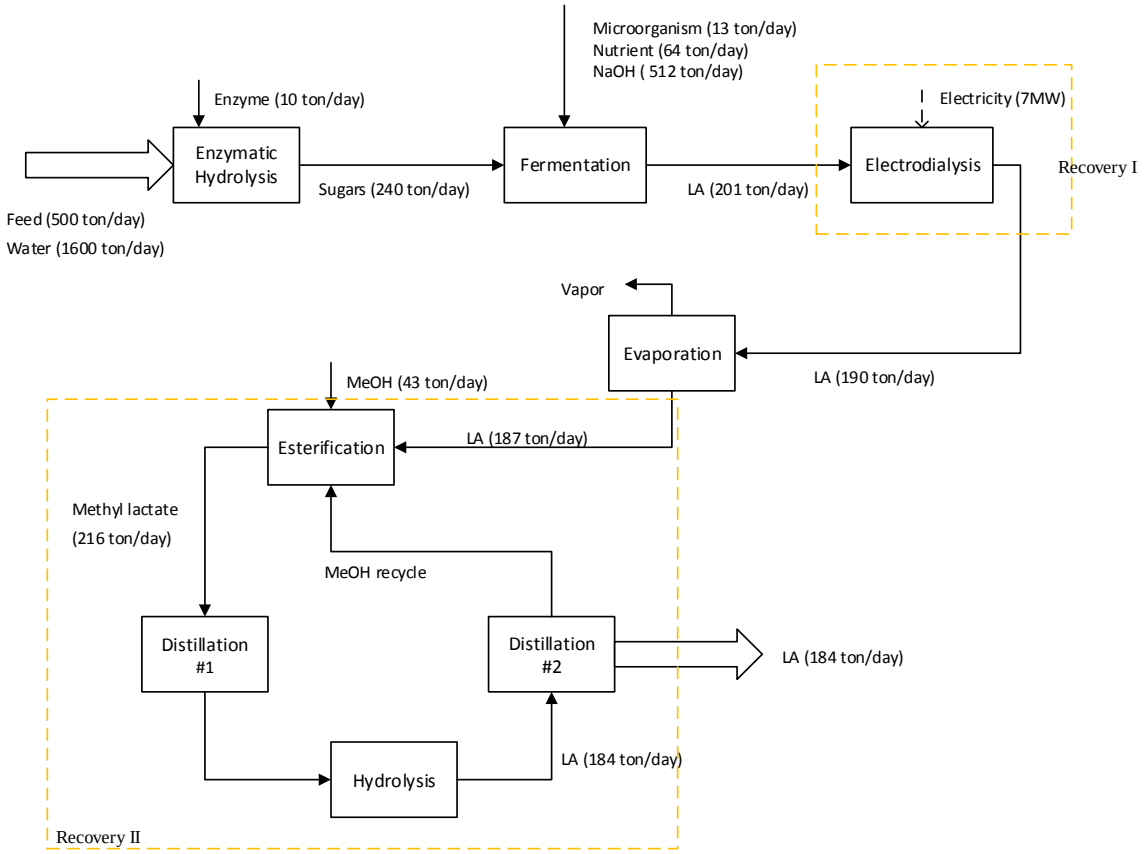


Figure 4-11 Material balance for the stand-alone bio-based lactic acid production with the recovery by electrodialysis (Project B)

Table 4-5 The most energy demanding units in the lactic acid production with the recovery by electrodialysis (Project B)

Unit	MW
Distillation #1	117.8
Distillation #2	58.7
Evaporation	141.6
Esterification	4.5
Hydrolysis	6.0

4.3.2 Stand-alone bio-based succinic acid production (Project C, D)

Figure 4-12 shows the results of the material balance obtained from the Aspen Plus simulation of the stand-alone bio-based succinic acid production with recovery by direct crystallization (Project C).

The same results of the enzymatic hydrolysis as those obtained in Section 4.3.1 were used here. In a similar way as in the bio-based lactic acid production, microorganisms, which metabolize sugars (glucose, xylose) and produce succinic acid as a major metabolite, were used during the fermentation maintaining the temperature at 37 °C and the pH at 7. During the fermentation, 182 ton/day of succinic acid are produced and a 76% (g SA/ g sugar) yield was obtained.

In Project C, the fermentation broth was evaporated and the succinic acid was crystallized by adding 0.17 ton/day of hydrochloric acid (HCl) and by decreasing the temperature to 4 °C. During the direct crystallization, 154 ton/day of succinic acid crystals with 85% yield (g SA_{cry}/ g SA) were produced before being sent to the Dryer. Table 4-6 presents the most energy demanding process steps in the stand-alone bio-based succinic acid production with the recovery by direct crystallization.

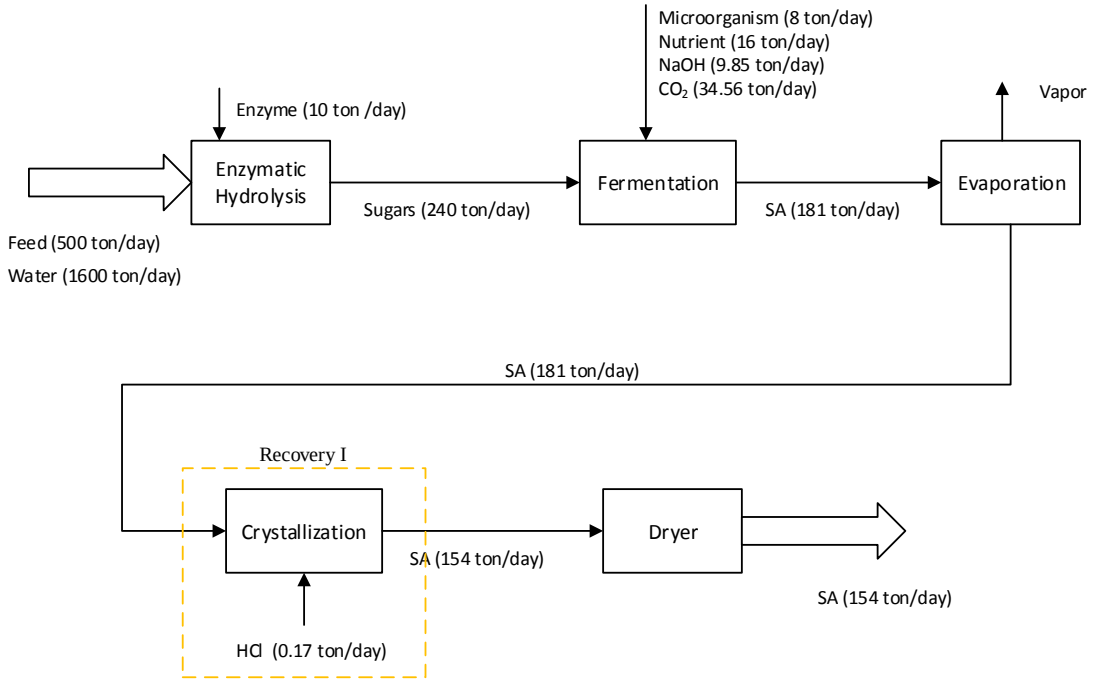


Figure 4-12 Material balance for the stand-alone bio-based succinic acid production with direct crystallization (Project C)

Table 4-6 The most energy demanding units in the succinic acid production with the recovery by direct crystallization (Project C)

Unit	MW
Evaporation	290.3
Dryer	5.0
Crystallization	14.0

The material balance based on the Aspen Plus simulation of the stand-alone bio-based succinic acid production with recovery by electrodialysis (Project D) is presented in Figure 4-13. The results of the enzymatic hydrolysis and the fermentation are the same as in Figure 4-12. For the recovery by electrodialysis, the succinic acid recovered from the fermentation broth was 163 ton/day, with 90 % yield. The supply of extra electricity for the electrodialysis is 6MW, which will be included in the economic evaluation. After the electrodialysis, the stream is evaporated and the succinic acid is crystallized by decreasing the pH and the temperature. The final succinic acid crystal production after drying was 154 ton/day, with a 30.8 % (g SA / g feedstock) yield.

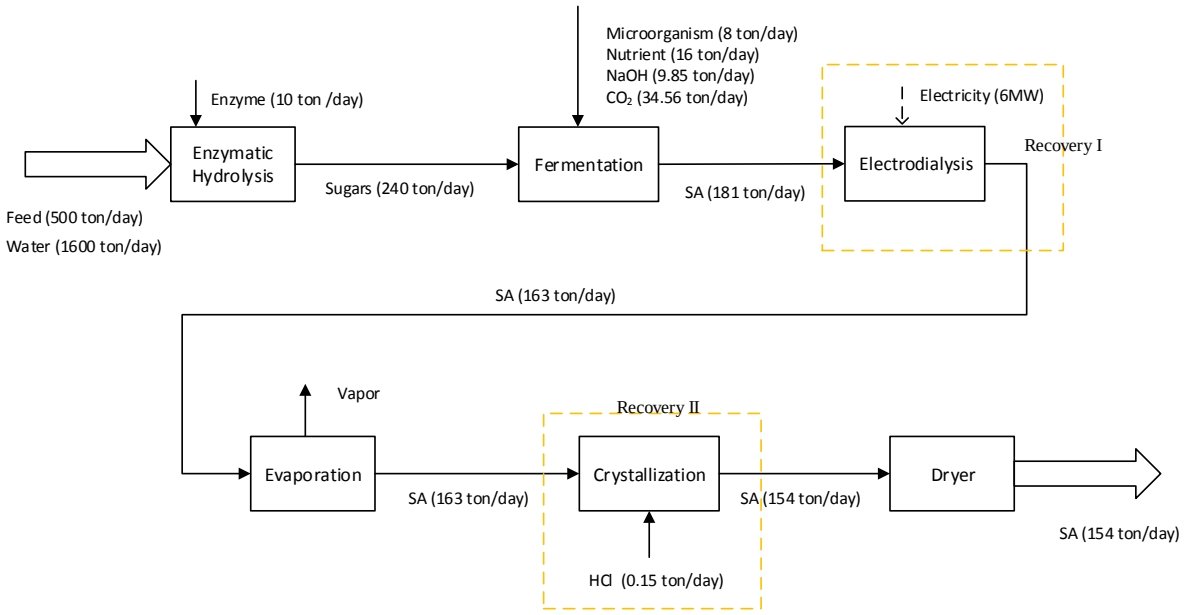


Figure 4-13 Material balance for the stand-alone bio-based succinic acid production with recovery of electrodialysis (Project D)

Table 4-7 The most energy demanding units in the succinic acid production with the recovery by electrodialysis (Project D)

Unit	MW
Evaporation	231.3
Dryer	5.0
Crystallization	14.0

4.4 Summary

In this project, five process steps for the production of bio-based lactic and succinic acid from hydrolysate of aspen chips were studied:

i. Pretreatment: To make the structure of lignocelllulosic biomass more sensitive and accessible in order to release to cellulose and hemicelluloses

ii. Enzymatic hydrolysis: To convert the cellulose and hemicelluloses to fermentable sugars (pentose, hexose)

iii. Detoxification: To remove the inhibitors formed during pretreatment and hydrolysis that hinder the fermentation

iv. Fermentation: To convert the sugars to lactic or succinic acid

v. Product recovery: To separate pure lactic or succinic acid from the fermentation broth

In this project two different configurations depending on the recovery method for each product (lactic and succinic acid) were selected and simulated on Aspen Plus:

- Project A: Bio-based lactic acid production with recovery by conventional method (precipitation)
- Project B: Bio-based lactic acid production with recovery by electrodialysis
- Project C: Bio-based succinic acid production with recovery by direct crystallization
- Project D: Bio-based succinic acid production with recovery by electrodialysis

Table 4-8 summaries the key results obtained from the simulation of the Projects A to D.

Table 4-8 Comparison of the material balances based on the simulation results

		Project A	Project B	Project C	Project D
Enzymatic hydrolysis	Feed	500 ton/day			
	Sugars	240 ton/day			
	Yield	48%			
		Lactic acid		**Succinic acid**	
Fermentation	Product	201 ton/day		182 ton/day	
	Yield	84%		76%	
Recovery I	Product	184 ton/day	190 ton/day	154 ton/day	163 ton/day
	Yield	92%	95%	85%	90%
Recovery II	Product	180 ton/day	184 ton/day	-	154 ton/day
	Yield	98%	97%	-	94%
Overall	Yield	36%	37%	30.8%	30.8%

In Project A and Project B, Recovery I indicates the precipitation and electrodialysis steps respectively, and Recovery II indicates the further purification process after the Recovery I that consists of esterification, distillation, and hydrolysis steps.

In Project C and Project D, Recovery I indicates the direct crystallization and electrodialysis steps respectively, and Recovery II indicates the crystallization step in Project D.

CHAPTER 5 TECHNO-ECONOMIC ANALYSIS OF THE INTEGRATED FOREST BIOREFINERY (IFBR)

5.1 Energy analysis of the IFBR

The Pinch Analysis and its analysis tools such as the Composite Curves (CC) and the Grand Composite Curve (GCC) were used to for the analysis of the IFBR. The process integration is composed of two steps that are described below (Figure 5-1).

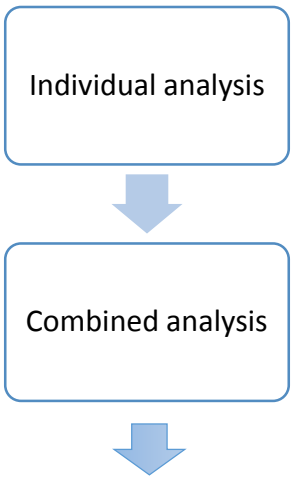


Figure 5-1 Process integration strategy

In scenario 1, HEN design of the stand-alone lactic acid and succinic acid plant is performed first. Secondly, the streams using hot utility, which are indicated as green arrows in Figure 5-2, are extracted. Then a new HEN design is carried out with those streams, hot streams from the TMP mill that are determined during the combined analysis, and hot utilities (Figure 5-3). In scenario 2, HEN design with all of streams of the stand-alone lactic or succinic acid plants, hot streams from the TMP mill that are determined during the combined analysis, and hot utilities is performed simultaneously (Figure 5-4).

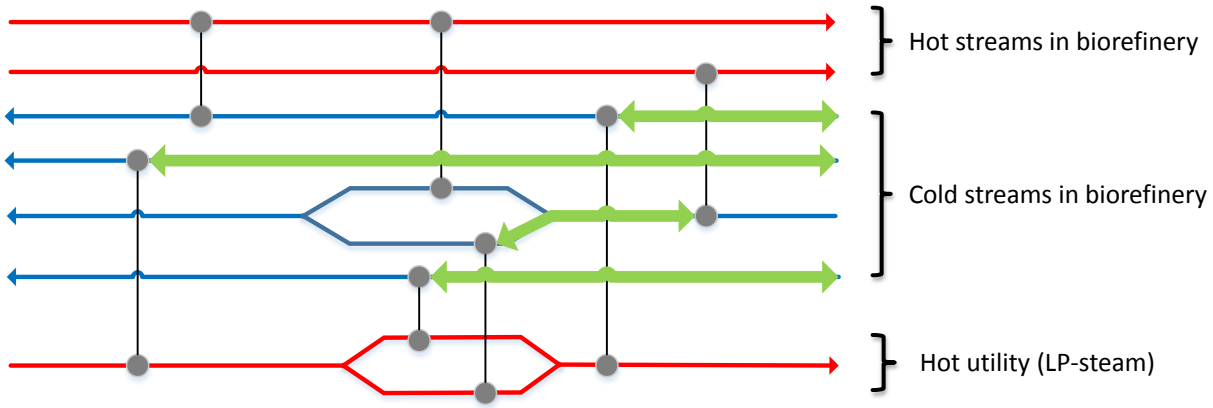


Figure 5-2 HEN design and heat recovery opportunity in scenario 1 (1)

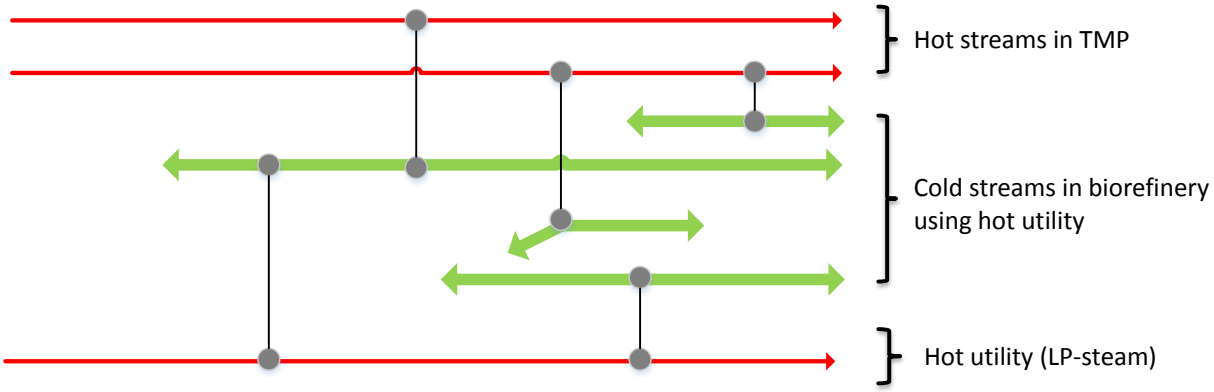


Figure 5-3 HEN design and heat recovery opportunity in scenario 1 (2)

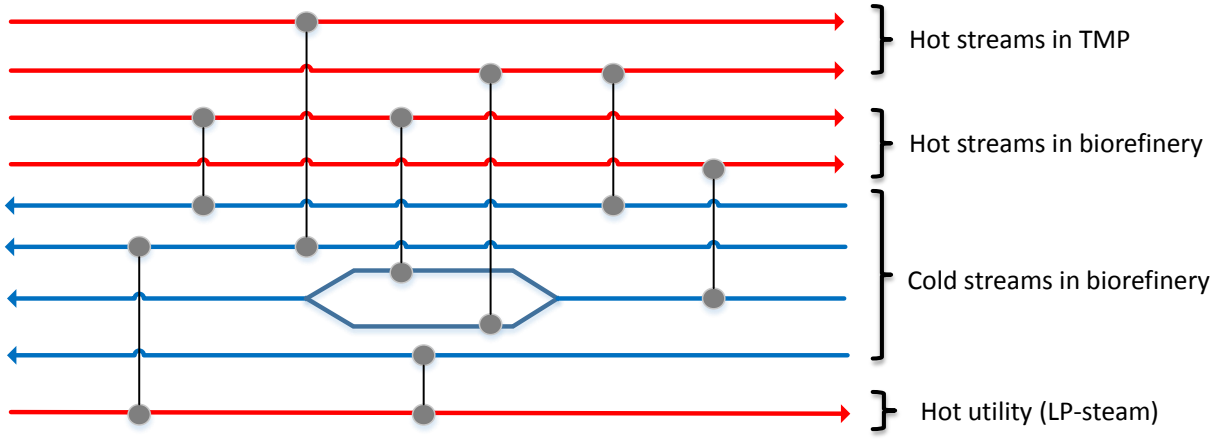


Figure 5-4 HEN design for the heat recovery opportunity in scenario 2

5.1.1 Individual analysis of TMP, LA, and SA processes

Pinch analyses on the TMP mill, lactic acid plant and succinic acid plant are performed separately. The streams data of the TMP mill such as heat load (ΔH), supply temperature (℃), target temperature (℃) were provided by FPInnovations and those for the lactic and succinic acid biorerinery were extracted from the Aspen Plus simulation. The streams were defined as either "hot" that require cooling or "cold" that require heating. The total energy requirement (energy target) and pinch point were determined using the Composite Curves. The utility level that should be provided for the process were obtained from the Grand Composite Curve. The temperature difference (ΔT_{min}) of 10℃ between the hot and cold curves was set. Aspen Energy Analyzer and Microsoft Excel were used to build the Composite Curves and Grand Composite Curve.

5.1.1.1 TMP mill

The relevant streams of the TMP mill were identified in Table B1 in Appendix B. The Composite Curves are shown in Figure 5-5, and the pinch point was obtained at 142.1℃ (ΔT_{min} was assumed to be 10℃). The minimum hot utility demand ($Q_{H,min}$ of 57 MW) and the minimum cooling utility demand ($Q_{C,min}$ of 14 MW) were determined in Figure 5-5.

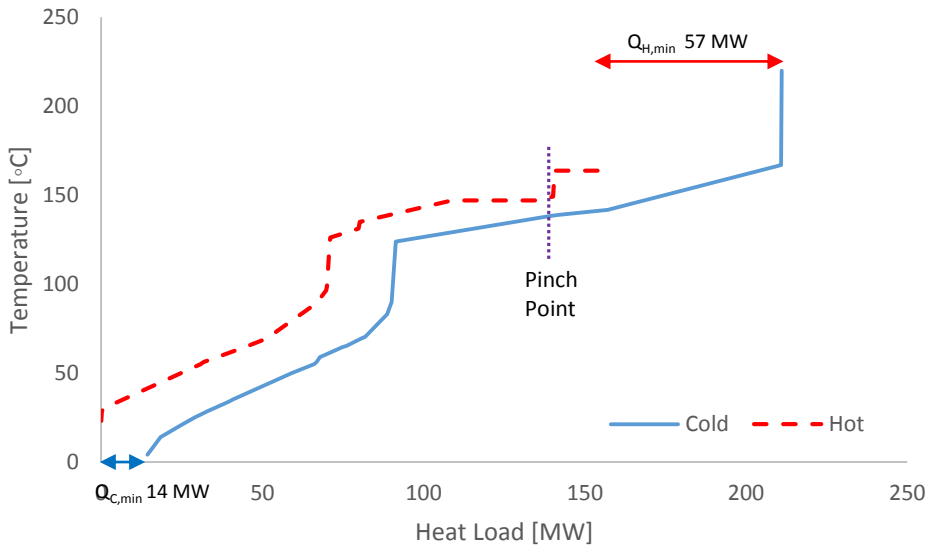


Figure 5-5 Composite curve of the TMP mill

5.1.1.2 Stand-alone bio-based lactic acid plant (Project A, B)

The Composite Curves of the bio-based lactic acid plant using 500 ton/day of aspen wood chips hydrolysate as a feed stock are shown in Figure 5-6. The streams data of the lactic acid biorefinery with the recovery by conventional method (precipitation, Project A) and electrodialysis (Project B) were extracted from the result of the Aspen Plus simulation (Table B2 and Table B3 in Appendix B). In project A, the pinch point was 94.9°C and the minimum heating demand ($Q_{H,min}$), the minimum cooling demand ($Q_{C,min}$) were determined as 209 MW and 40 MW, respectively. In project B, the pinch point was set to 95.1 °C, and the minimum heating demand ($Q_{H,min}$) and the minimum cooling demand ($Q_{C,min}$) were 305 MW and 90 MW respectively.

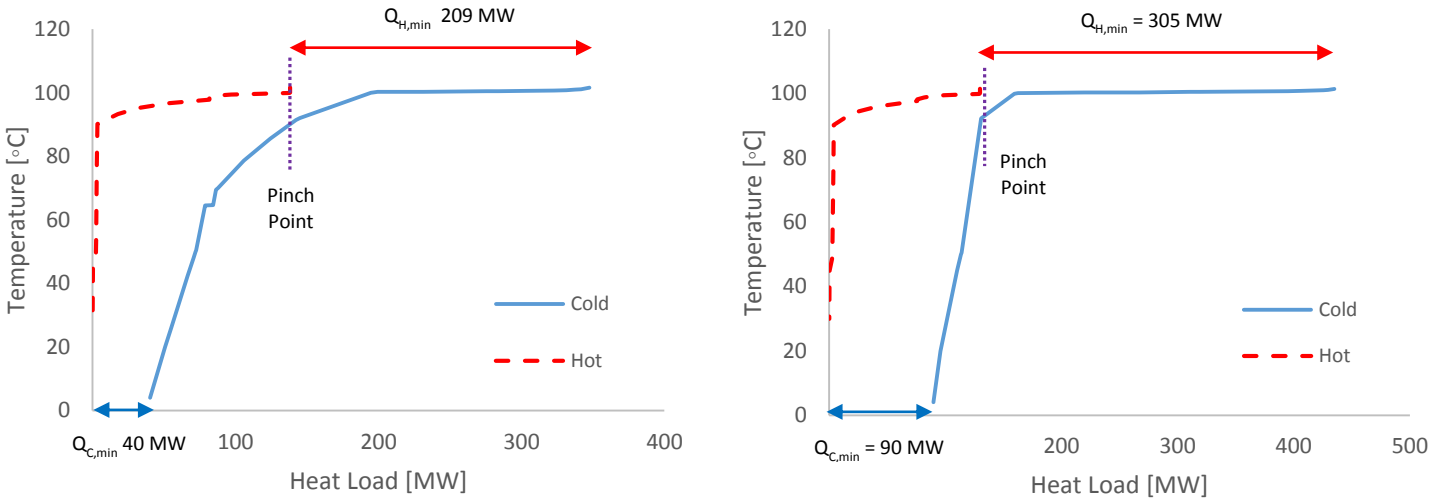


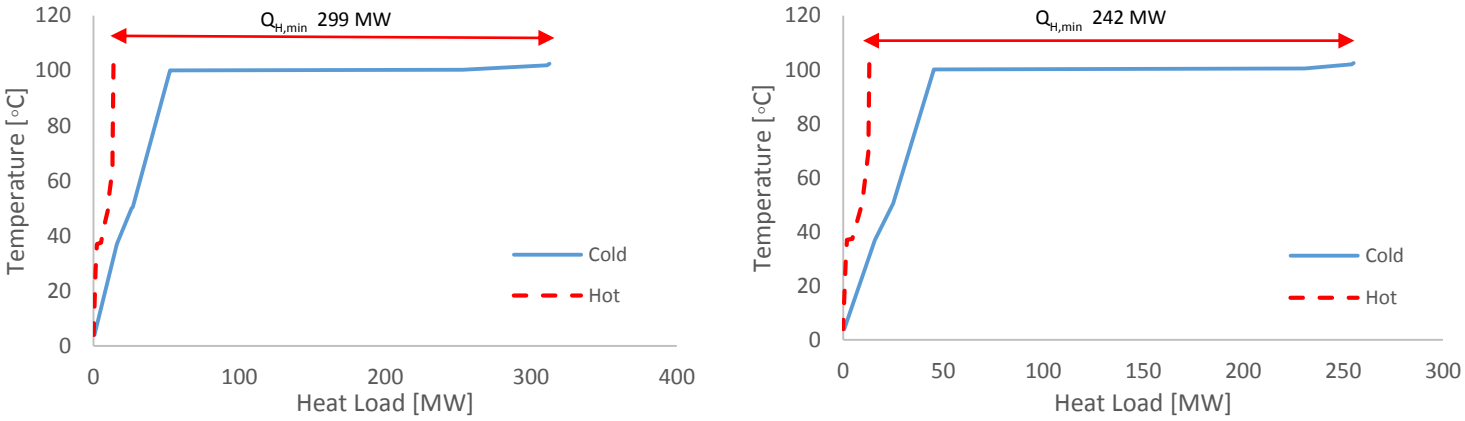
Figure 5-6 Composite curves of the stand-alone bio-based lactic acid plant

A) Project A: recovery by conventional method, B) Project B: recovery by electrodialysis

5.1.1.3 Stand-alone bio-based succinic acid plant (Project C, D)

The Composite Curves of the stand-alone bio-based succinic acid plant using 500 ton/day of aspen wood chips hydrolysate as a feed stock with the recovery by direct crystallization (Project C) and electrodialysis (Project D) are shown in Figure 5-7. The related stream data are represented in Table B4 and Table B5 in Appendix B. As can be seen in Figure 5-7, both processes have a 9 °C pinch

point and very little cooling demand. The minimum heating demand ($Q_{H,min}$) of the stand-alone bio-based succinic acid production with recovery by direct crystallization and elctrodialysis are determined 299 MW and 242 MW, respectively.



(A) **(B)**

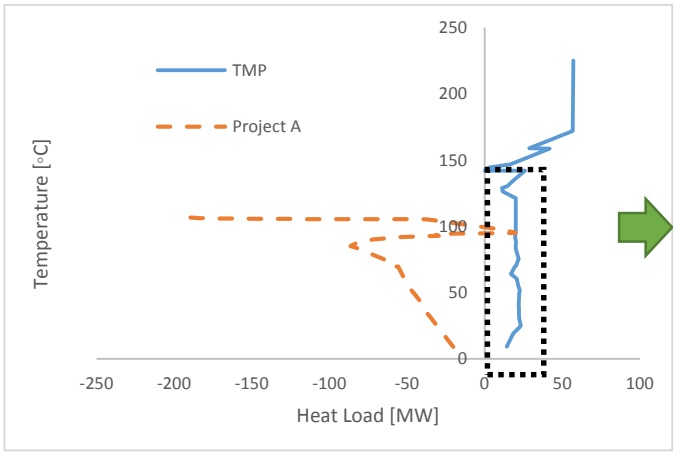
Figure 5-7 Composite curves of the stand-alone bio-based succinic acid plant

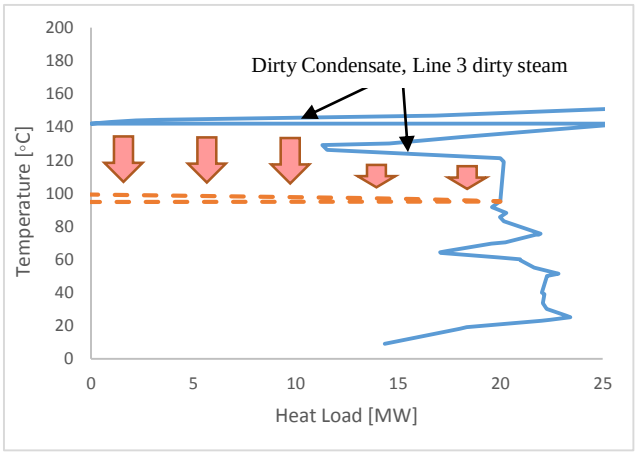
A) Project C: recovery direct crystallization, B) Project D: recovery by electrodialysis

5.1.2 Combined analysis

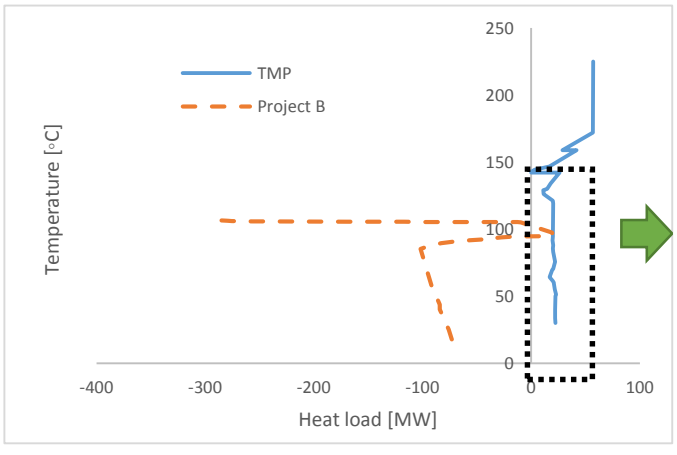
In order to identify the possible heat transfers from the TMP mill to the lactic or succinic acid plant, the combination of the Grand Composite Curves was used. The combined GCCs between the TMP mill and the project A to D are represented in Figure 5-8. It was found that heat from TMP mill can be transferred to lactic or succinic acid plant. Specifically two streams in the TMP mill were determined as potential hot sources: The Dirty condensate and the Line 3 dirty steam. These two streams are the dirty steam produced in the refiners of the TMP process, then sent to the reboilers to be cleaned.

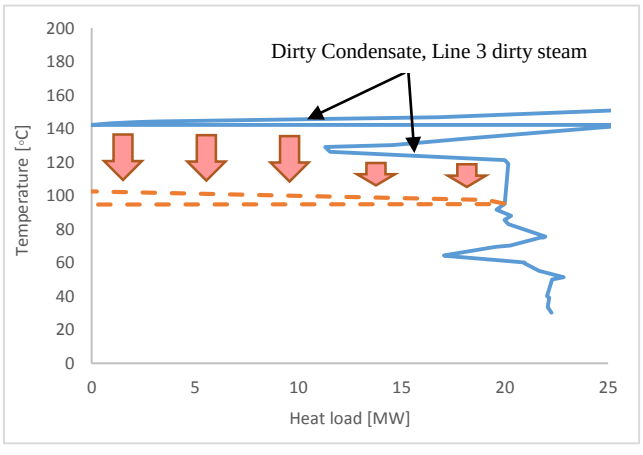
(A)


TMP
Project A
Temperature [°C]
Heat Load [MW]
250
200
150
100
50
0
-250
-200
-150
-100
-50
0
50
100

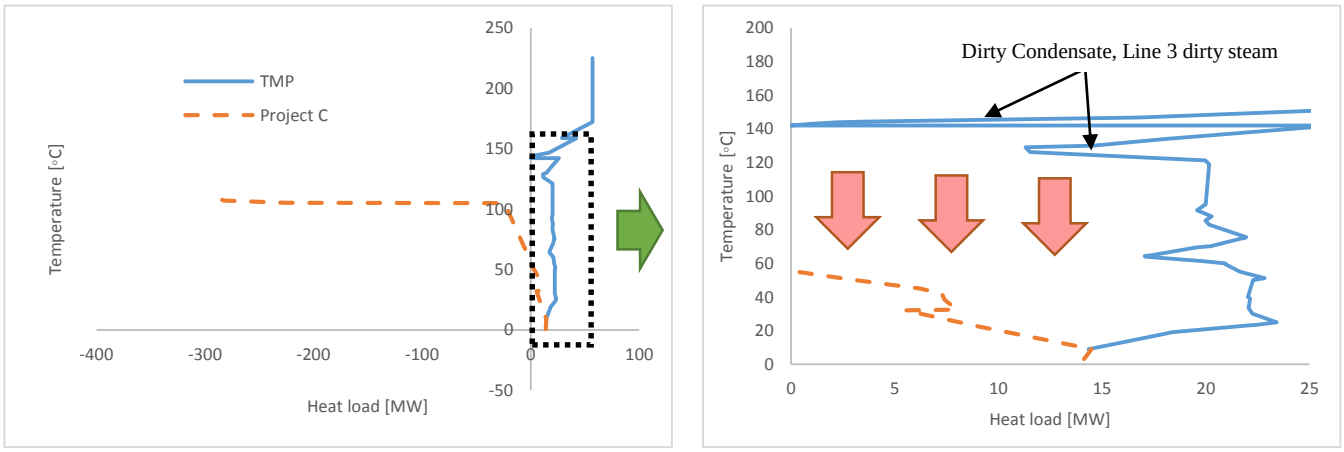

Dirty Condensate, Line 3 dirty steam
Temperature [°C]
Heat Load [MW]
200
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25

(B)


TMP
Project B
Temperature [°C]
Heat load [MW]
250
200
150
100
50
0
-400
-300
-200
-100
0
100


Dirty Condensate, Line 3 dirty steam
Temperature [°C]
Heat load [MW]
200
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25

(C)



(D)

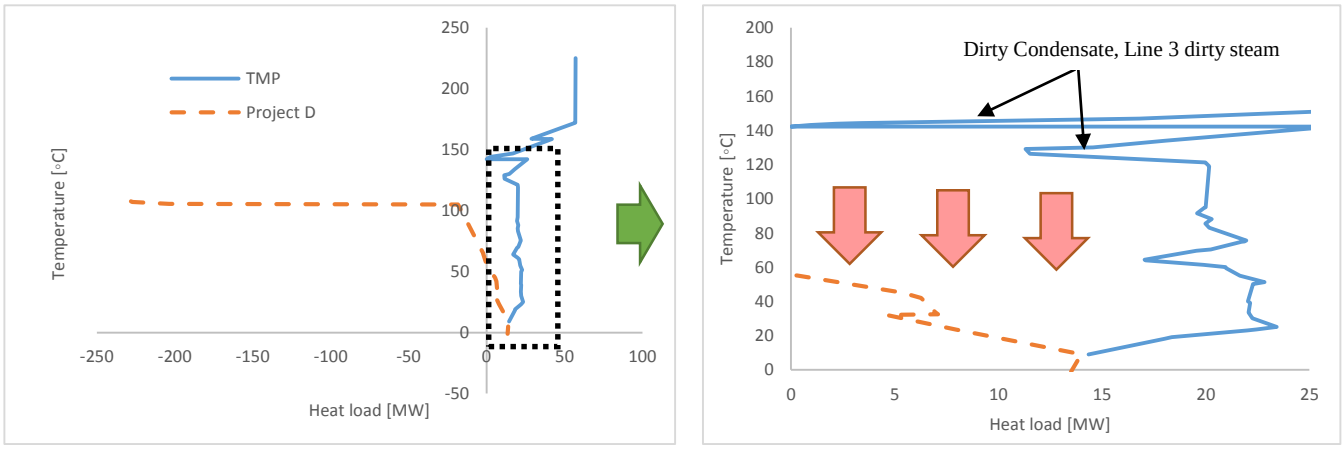


Figure 5-8 Combined GCC of the TMP mill and the biorefinery

A) Project A: LA production with recovery by conventional method

B) Project B: LA production with recovery by electrodialysis

C) Project C: SA production with recovery by direct crystallization

D) Project D: SA production with recovery by electrodialysis

5.1.3 Heat recovery opportunities of the IFBR

In order to identify the heat recovery opportunities of the IFBR, the Heat Exchanger Network (HEN) design was performed for the four projects in two scenarios. Project A to D are integrated to the TMP mill, and the integrated forest biorefineries are defined in Figure 5-9.

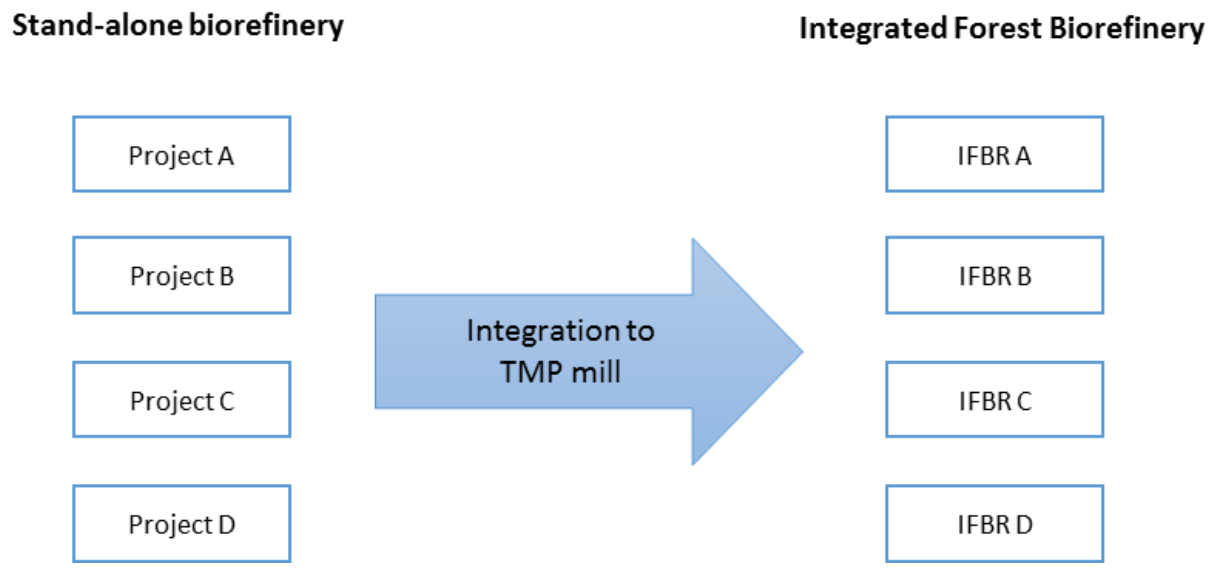


Figure 5-9 Integrated forest biorefineries

- IFBR A : Integration of the bio-based lactic acid plant with the recovery by conventional method to the TMP mill
- IFBR B : Integration of the bio-based lactic acid plant with the recovery by electrodialysis to the TMP mill
- IFBR C : Integration of the bio-based succinic acid plant with the recovery by direct crystallization to the TMP mill
- IFBR D : Integration of the bio-based succinic acid plant with the recovery by electrodialysis to the TMP mill

5.1.3.1 Integration of the bio-based lactic acid plant with recovery by conventional method to the TMP mill (IFBR A)

The total heat requirement in the stand-alone bio-based lactic acid plant with the recovery by conventional method is 367.6MW. The possible heat recovery options are presented in Figure 5-11 and Figure 5-11. In the stand-alone bio-based lactic acid plant with the recovery by conventional method, the 0.5 MW of LP-steam used to heat the H_2SO_4 supply for the precipitation can be completely substituted by the Dirty condensate stream. The crude LA from the precipitation step is heated before the evaporation step using LP steam (18MW). Steam savings of 1.7 MW can be

achieved by using the heat from the Dirty Condensate stream after the integration. The LP-steam used to heat the methanol supply to the esterification step (0.3MW) was recovered by the stream of Dirty condensate. For the heating in the esterification step, 11MW of LP-steam is needed in the stand-alone Project A. After the integration, 0.3 MW of heat was recovered from the Dirty Condensate stream. The heating of the reboiler of the distillation unit consumes 58.41MW of LP-steam. Thanks to the integration, 32.85 MW of heat was recovered by the stream of Line 3_Dirty steam.

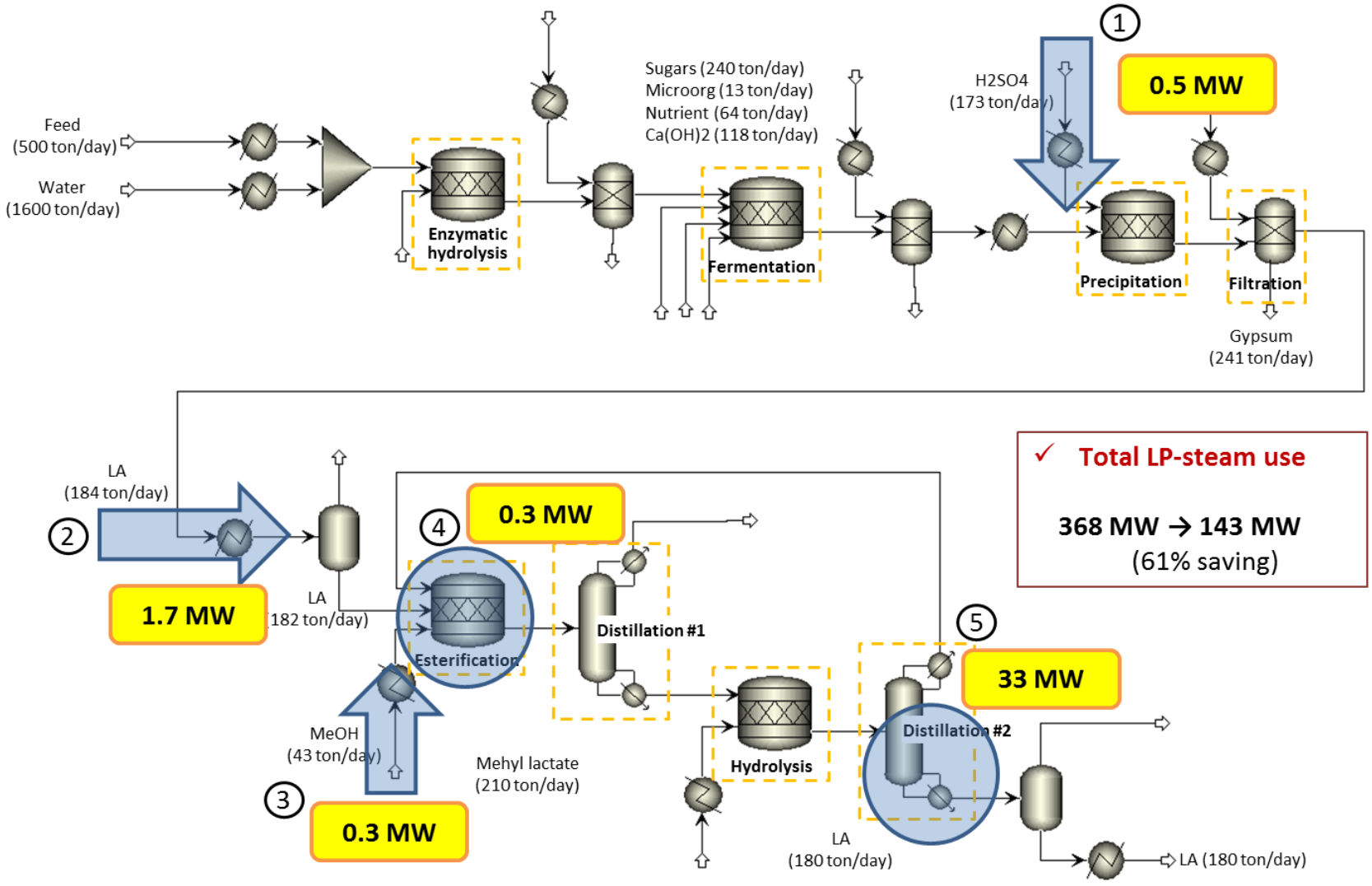
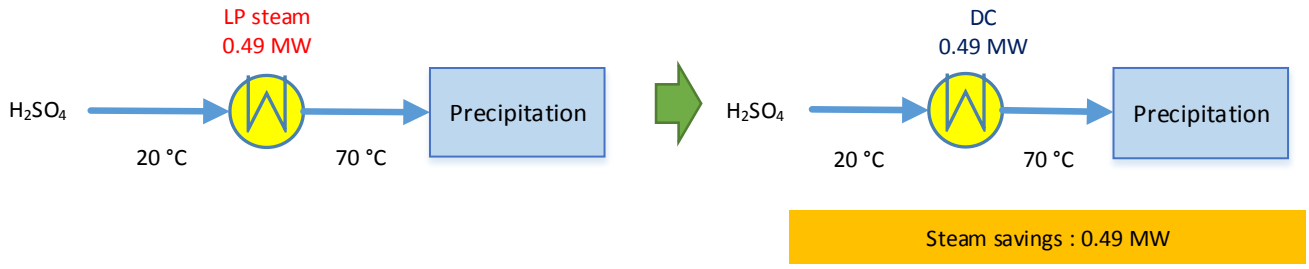


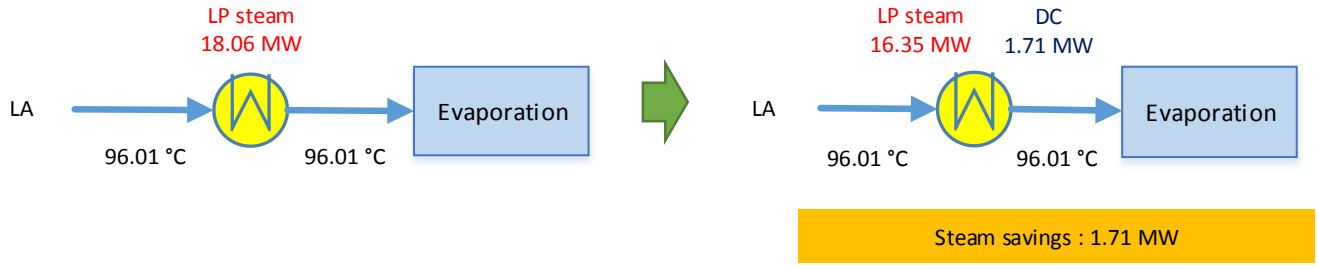
Figure 5-10 Heat recovery opportunities in the IFBR A

Project A (stand-alone)	IFBR A

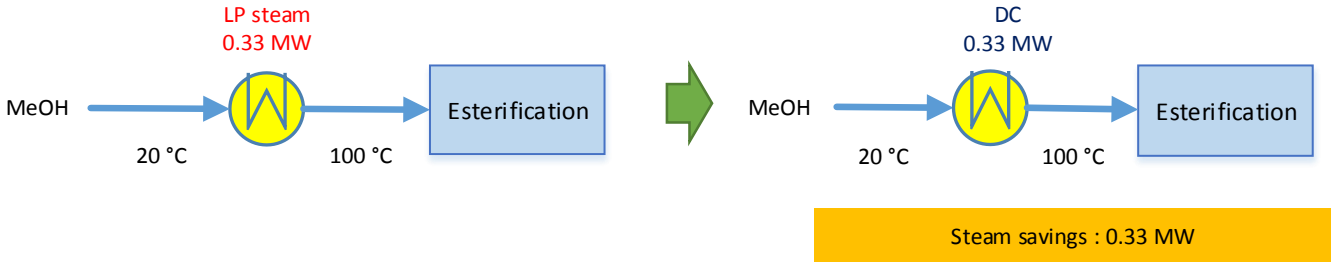
1. H_2SO_4 supply to the precipitation



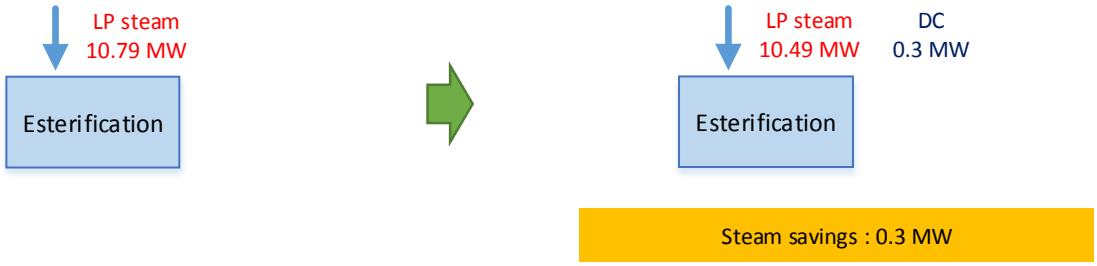
2. Crude LA from the precipitation



3. H_2SO_4 supply to the precipitation



4. Heating for the esterification



5. Heating for the reboiler in distillation #2

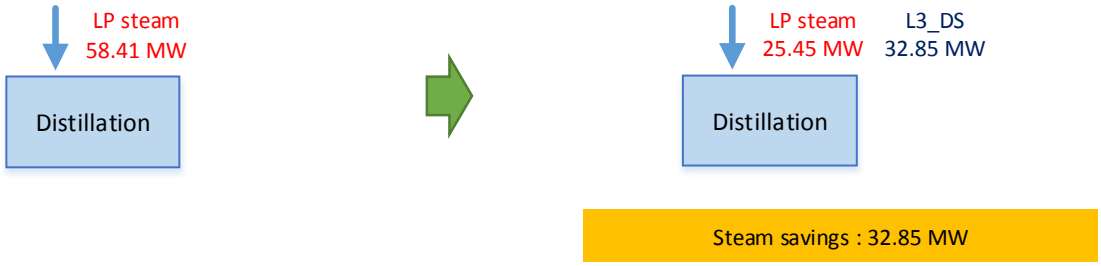


Figure 5-11 Comparisons of the LP steam consumptions between the project A (stand-alone) and the IFBR A

(DC: Dirty condensate, L3_DS: Line3_Dirty steam)

In scenario 1, the streams using LP-steam in the lactic acid biorefinery were extracted and a new HEN was designed with the following streams, two hot streams from the TMP mill (Dirty condensate and Line 3 dirty steam), and LP-steam. In the scenario 2, the HEN design was performed with all the streams at the same time. The LP-steam demand was decreased to 143.4 MW and 144.1 MW after the heat integration in scenario 1 and 2 respectively (Table 5-1). Finally the 61% of total steam savings compared to the stand-alone project A were obtained.

Table 5-1 Energy profile of the IFBR A (integration of LA plant with recovery by conventional method to the TMP mill)

Heat sources		Load [MW]	
		Scenario 1	**Scenario 2**
Heat recovery	Dirty condensate	2.83	4.30
	Line 3_Dirty steam	32.96	32.96
External heating	LP-STEAM	143.36	144.14
Steam savings		61%	

5.1.3.2 Integration of the bio-based lactic acid plant with recovery by electrodialysis to the TMP mill (IFBR B)

In the case of the stand-alone lactic acid plant with the recovery by electrodialysis, the total heat requirement is 351.1 MW. The possible heat recovery opportunities by the integration are shown in Figure 5-12 and Figure 5-13. In the stand-alone bio-based lactic acid plant with recovery by electrodialysis, the LP-steam use for the methanol heating before the esterification step (0.33MW) can be recovered by the Dirty condensate stream. In the esterification step, 13.35 MW of LP-steam is needed to heat the esterification reactor. After the integration, 1.72 MW of heat was recovered from the stream of Dirty Condensate. To heat the reboiler of the distillation unit 84.3 MW of LP-steam are required. As a result of the integration, 33 MW of heat can be recovered using the Line 3_Dirty steam.

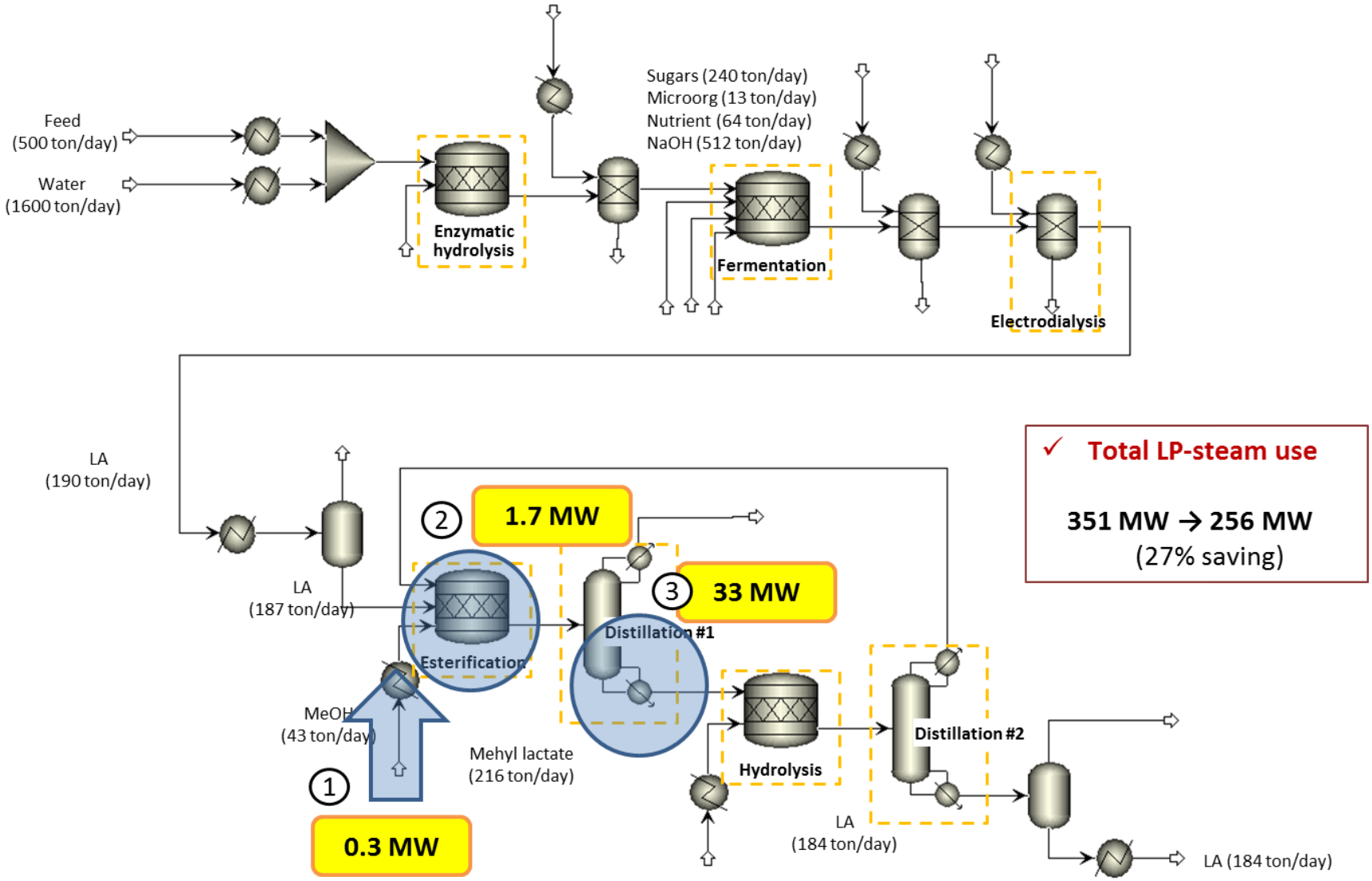
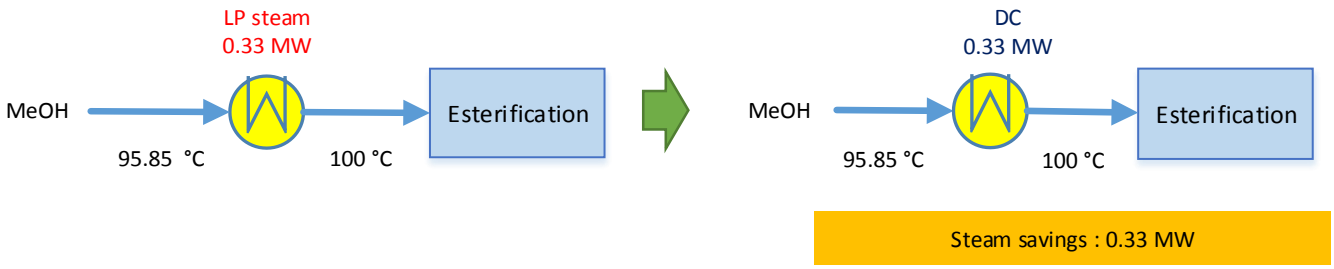


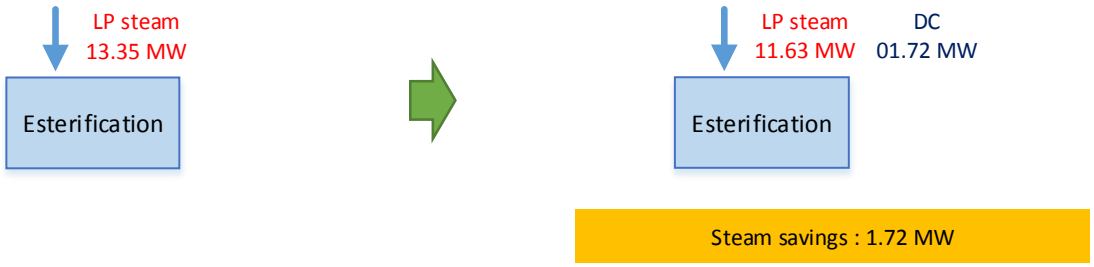
Figure 5-12 Heat recovery opportunities in the IFBR B

Project B (stand-alone)	IFBR B

1. MeOH supply to Esterification



2. Heating for the esterification



3. Heating for the reboiler in distllation #1

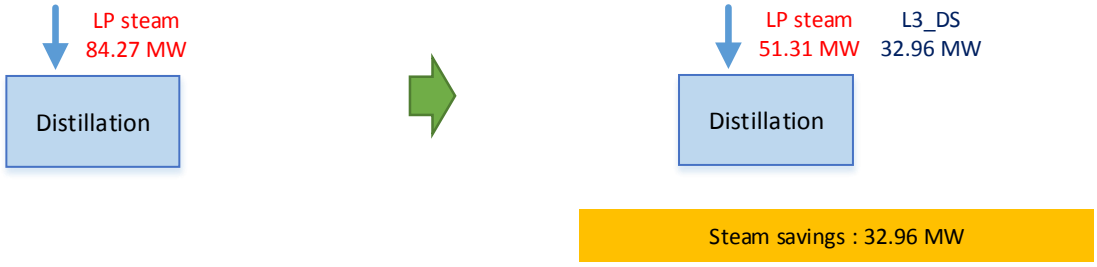


Figure 5-13 Comparisons of the LP steam consumptions between the project B (stand-alone) and the IFBR B

(DC: Dirty condensate, L3_DS: Line3_Dirty steam)

It was shown that 35 MW and 37.3 MW of internal heat is recovered during the heat integration from the TMP mill in scenarios 1 and 2 respectively, and the final LP-steam consumption was decreased to 255.7 MW, which means 27% of steam reduction, in both scenario 1 and 2 (Table 5-2)

Table 5-2 Energy profile of the IFBR B (integration of LA plant with recovery by electrodialysis to the TMP mill)

Heat sources		**Load [MW]**	
		Scenario 1	**Scenario 2**
Heat recovery	Dirty condensate	2.05	4.30
	Line 3_Dirty steam	32.96	32.96
External heating	LP-STEAM	255.71	255.71
Steam saving		27 %	

5.1.3.3 Integration of the bio-based succinic acid plant with recovery by direct crystallization to the TMP mill (IFBR C)

The total heat requirement in the stand-alone bio-based succinic acid plant with the recovery by direct crystallization is 330.4 MW. The opportunities for heat recovery by integration are presented in Figure 5-14 and Figure 5-15. The water supply to the filtration step after the enzymatic hydrolysis requires 5.3 MW of LP-steam. The integration allows 2.18 MW of heat to be recovered from the Dirty Condensate stream. The water supply to the filtration after the fermentation also requires 4.07 MW of LP-steam; it is possible to recover 1.15 MW of heat from the Dirty Condensate stream. Crude SA produced from the fermentation step is heated before the evaporation step using LP steam (290.32 MW). As a result of the integration, 32.96 MW of heat can be recovered using the Line 3_Dirty steam. For the air heating in the drying step, 0.96MW of LP-steam is needed in the stand-alone project C. After the integration, this heat can be recovered from the Dirty Condensate steam.

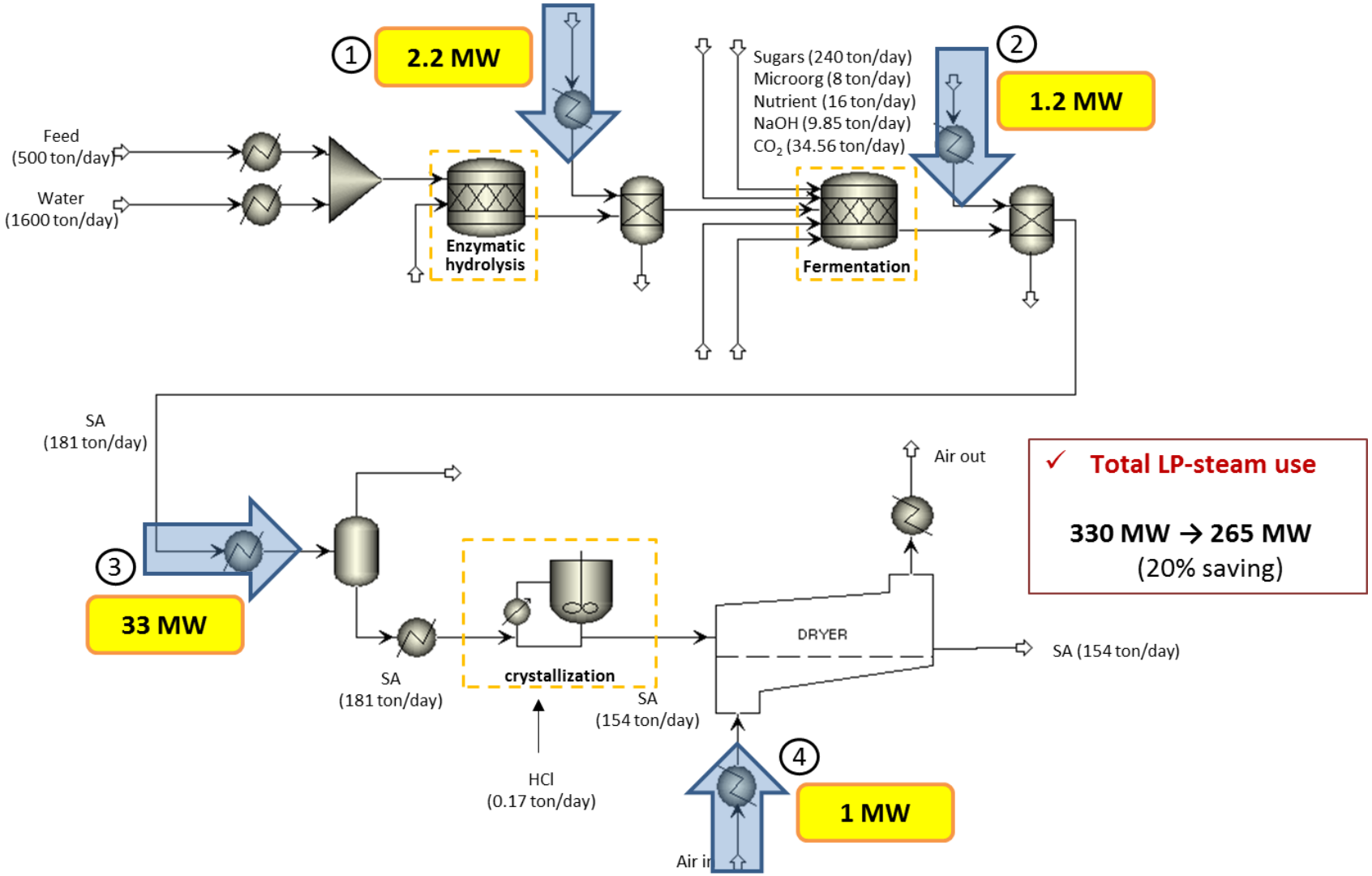


Figure 5-14 Heat recovery opportunities in the IFBR C

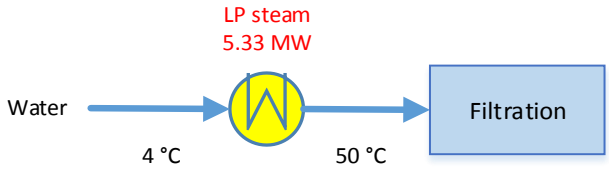
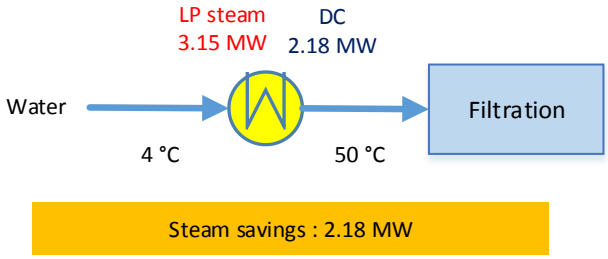
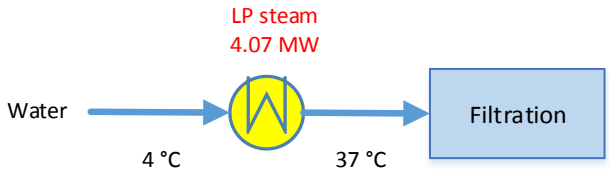
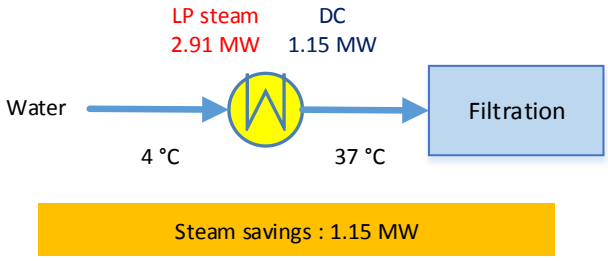
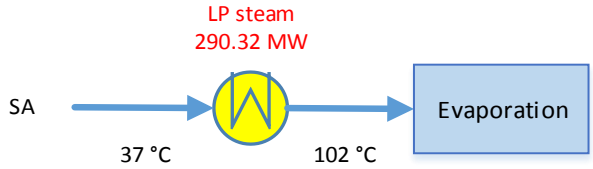
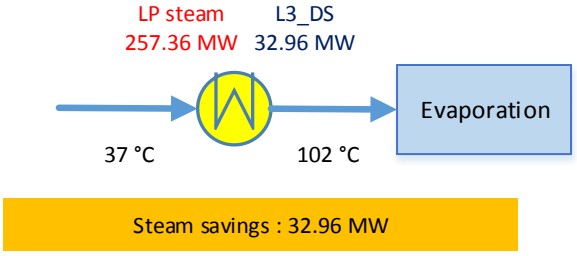
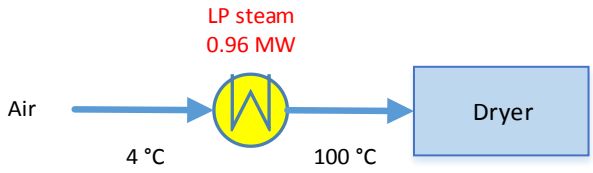
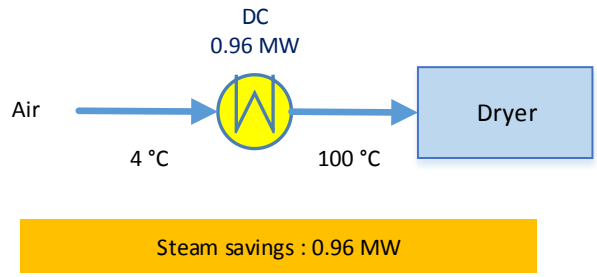
Project C (stand-alone)	IFBR C
1. Water supply to the Filtration after the enzymatic hydrolysis	
	
2. Water supply to the Filtration after the fermentation	
	
3. Crude SA to the evaporation	
	
4. Air to the dryer	
	

Figure 5-15 Comparisons of the LP steam consumptions between the project C (stand-alone) and the IFBR C (DC: Dirty condensate, L3_DS: Line3_Dirty steam)

As a result of the heat integration, 37.26 MW of heat can be recovered from the TMP mill and the final LP-steam requirement is set to 265.63 MW (20% of steam saving) in both scenario 1 and 2 (Table 5-3)

Table 5-3 Energy profile of the IFBR C (integration of SA plant with recovery by direct crystallization to the TMP mill)

Heat sources		**Load [MW]**	
		Scenario 1	**Scenario 2**
Heat recovery	Dirty condensate	4.30	4.30
	Line 3_Dirty steam	32.96	32.96
External heating	LP-STEAM	265.63	265.63
Steam saving		20%	

5.1.3.4 Integration of the bio-based succinic acid plant with recovery by direct crystallization to the TMP mill (IFBR D)

The total heat requirement in the stand-alone bio-based succinic acid plant with recovery by direct crystallization is 270.9 MW. The heat recovery opportunities by integration are presented in Figure 5-16 and Figure 5-17. In the stand-alone project D, the water supply to the enzymatic hydrolysis needs 3.3 MW of LP-steam; this heat can also be recovered from the Dirty Condensate stream. The water supply to the filtration after the enzymatic hydrolysis also requires 3.52 MW of LP-steam. In this case, 1 MW of heat may be recovered by the Dirty Condensate. Crude SA produced from the fermentation step is heated before the evaporation step, which requires 290.32 MW of LP-steam. After the integration, 32 MW of heat can be recovered using the Line 3_Dirty steam. 0.96MW of LP-steam is needed for the air heating in the dryer step. After the integration, this heat can be recovered from the Dirty Condensate stream.

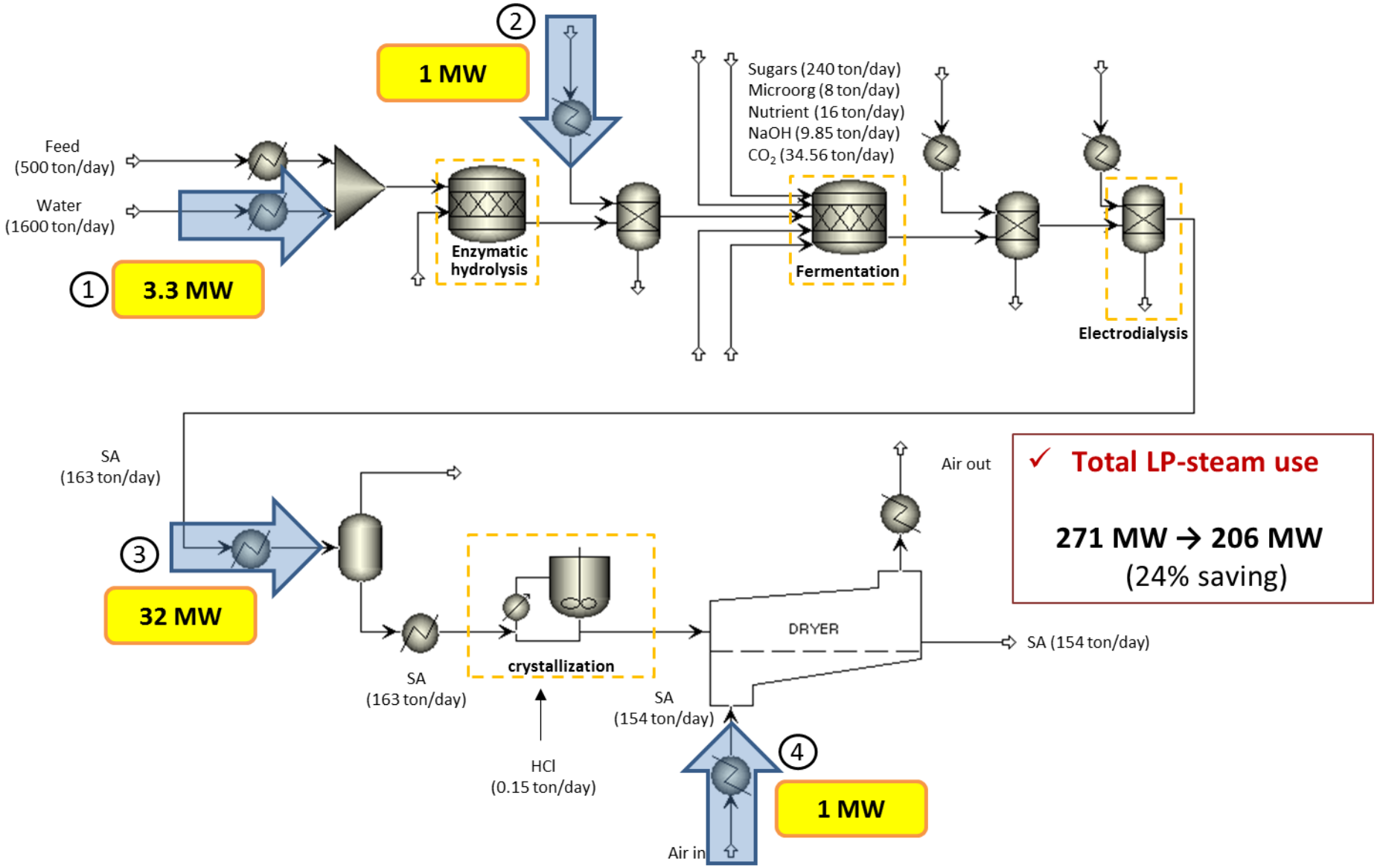


Figure 5-16 Heat recovery opportunities in the IFBR D

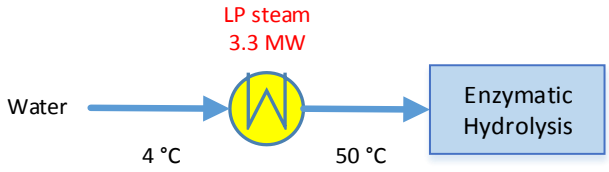
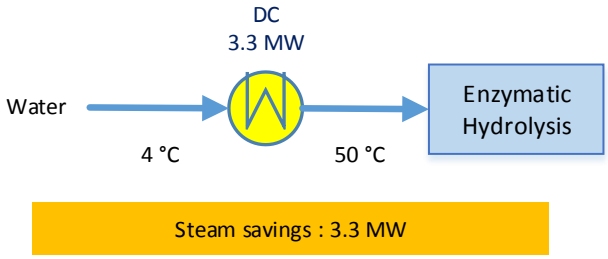
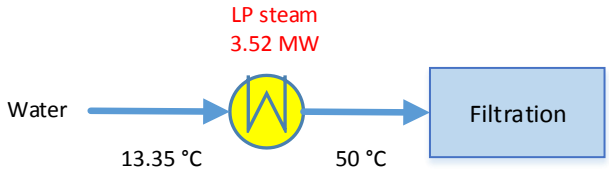
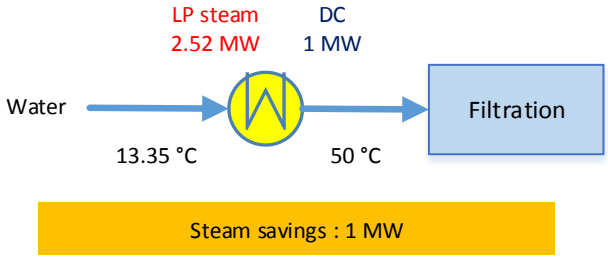
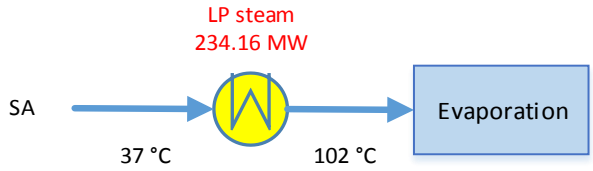
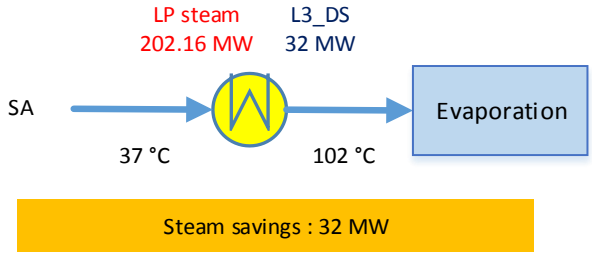
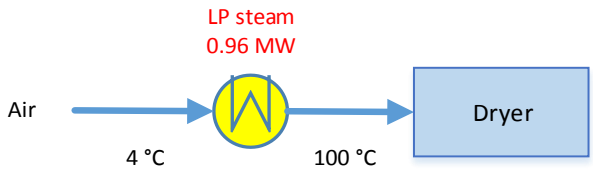
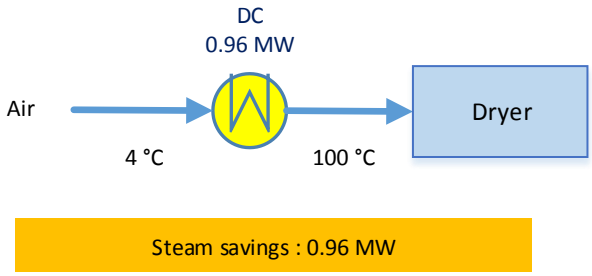
Project D (stand-alone)	IFBR D
1. Water supply to the enzymatic hydrolysis	
	
2. Water supply to the filtration after the enzymatic hydrolysis	
	
3. Crude SA to the evaporation	
	
4. Air to the dryer	
	

Figure 5-17 Comparisons of the LP steam consumptions between the project D (stand-alone) and the IFBR D (DC: Dirty condensate, L3_DS: Line3_Dirty steam)

As a result of the heat integration, 37.26 MW of internal heat can be recovered from the TMP mill, thus decreasing the LP-steam to 205.80 MW (24% of total steam saving) in both scenario 1 and 2 (Table 5-4).

Table 5-4 Energy profile of the IFBR D (integration of SA plant with recovery by electrodialysis to the TMP mill)

Heat sources		**Load [MW]**	
		Scenario 1	**Scenario 2**
Heat recovery	Dirty condensate	4.30	4.30
	Line 3_Dirty steam	32.96	32.96
External heating	LP-STEAM	205.80	205.80
Steam saving		24%	

5.1.3.5 Summary of the heat integration results

Thanks to the heat integration of the bio-based lactic and succinic acid plants with the TMP mill, the final LP-steam consumption has been decreased. There were little differences in the amount of possible heat recovery between scenarios 1 and 2. The details of LP-steam use in the stand-alone lactic and succinic plant and the integrated biorefinery in scenario 1 and 2 are shown in Figure 5-18. The results show that external utility (LP-steam) demand was reduced by 61%, 27%, 20%, and 24% in the IFBR A to D respectively.

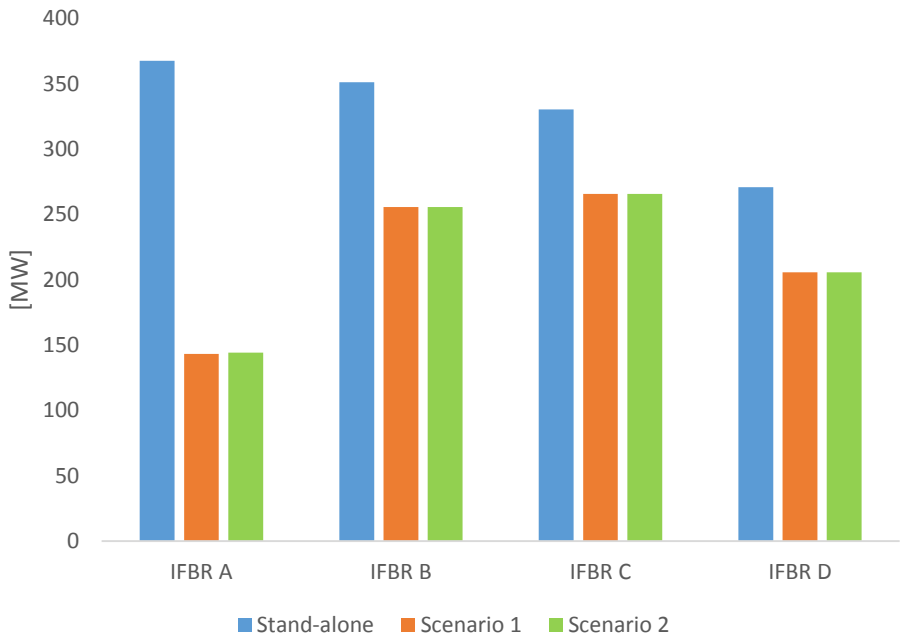


Figure 5-18 Comparison of LP-steam consumption in the various IFBRs and scenarios

The same result of heat integration was highlighted in scenario 1 and 2 in terms of additional LP-steam use. However, it was found that the total HEX area is different in scenario 1 and 2. The comparison of HEX area between the various projects and scenarios is shown in Figure 5-19. In IFBR A and scenario 1, the total HEX area was calculated as 33 200 m^2, which is 4 560 m^2 more than in scenario 2. In IFBR B, 41 334 m^2 of total HEX area was obtained, which is 6 330 m^2 more than in scenario 2. In IFBR C, on the other hand, the total HEX area in scenario 1 was 52 430 m^2, which is 130 m^2 less than in scenario 2. In IFBR D, the total HEX area in scenario 1 was 42 900 m^2, which is 461 m^2 less than in the scenario 2. The HEX network of each project and scenario are listed in Appendix C.

In conclusion, the heat integration of the biorefinery processes, which produce lactic or succinic acid, into the TMP mill allows the reduction of steam use comparing to the stand-alone biorefinery. The amount of possible heat recovery was similar for scenario 1 and 2. However, it was found that the HEX area may differ depending on the scenario.

Figure 5-19 Comparison of HEN area in the various IFBRs and scenarios

5.2 Economic evaluation

5.2.1 Total capital cost estimation

A preliminary evaluation of the economic feasibility of the lactic and succinic acid production was made. The total capital costs for the bio-based lactic and succinic acid plants that are integrated into the TMP mill were estimated and the results are shown in Table 5-5. The total capital cost of each project is calculated by summing the individual equipment costs (such as reactors, separators, and distillations) and the HEX costs. The detailed calculation of the capital costs is presented in Appendix D. The results show that the HEX network has a great impact on the total capital cost. The HEX between the reboiler and the LP-steam requirement in the distillation are not considered in the HEX costs as it is already included in the equipment cost of the distillation unit. Additional investment costs, such as warehouse, a site development, and an office construction are not considered in the economic analysis because the TMP mill will share its existing facility.

Table 5-5 Total capital cost estimation for the four IFBRs

	Equipment cost [M$]	HEX cost [M$]		Total [M$]	
		Scenario 1	Scenario 2	Scenario 1	Scenario 2
IFBR A	12	96	75	108	88
IFBR B	11	125	105	136	116
IFBR C	5	205	206	209	210
IFBR D	5	146	149	151	153

5.2.2 Annual operating cost estimation

The operating cost consists of fixed costs that include labor, maintenance fee, general overheads and variable costs of raw materials, waste handling, required chemicals, and utilities.

The specific data of salaries on the 1998 basis were taken from the NREL report [55] and were indexed to 2015. The index used for this adjustment was taken from the Bureau of Labor Statistics [104]. A fraction of 50% of the total salaries was included in the operating cost considering that the integrated biorefinery can share manpower with the existing TMP mill. General overhead costs, annual maintenance costs, and insurance & taxes were assumed to be 60% of total salaries, 2% of the installed equipment cost, and 1.5% of the installed equipment cost, respectively [55].

The variable operating costs for the enzymes, chemicals, and waste handling were taken from the literature [55, 105]. The feedstock price was assumed free as the prehydrolysate is provided by the TMP mill. As for the electricity use, only the additional electricity demands for the electrodialysis are considered. The cost of electricity and LP-steam are 7.96 ¢/kWh (average industrial electricity price in Canada, 2013) [106] and 0.7¢/MJ (calculation based on the natural gas price), respectively.

Table 5-6 presents the assumed prices for the operating cost estimation. The annual operating costs estimation of the four integrated bio-refineries are presented in Table 5-7 (see Appendix E for the detailed calculation).

Table 5-6 Assumed prices for the annual operating cost

	Price	Unit	Reference
Feedstock	0	$/ton	
Enzyme	0.0552	$/lb	[55]
Microorganism	0.024885	$/kg	[105]
Nutrient	0.0804	$/lb	[55]
$Ca(OH)_2$	0.0348	$/lb	[55]
H_2SO_4	0.0124	$/lb	[55]
Gypsum disposal	0.0094	$/lb	[55]
MeOH	416	$/ton	[107]
NaOH	400	$/ton	[55]
Membrane replace	439	$/year	[3]
Electricity usage	0.0796	¢/kWh	[106]
LP-steam	0.007	$/MJ	Provided from FPInnovations

Table 5-7 Annual operating cost estimation for the four integrated processes

	Scenario 1 [M$]	Scenario 2 [M$]
IFBR A	20	19
IFBR B	27	26
IFBR C	30	30
IFBR D	24	24

5.2.3 Annual revenue estimation

The sources of revenues are from selling the lactic and succinic acid produced. The selling prices of lactic and succinic acid were assumed to be 2300 $/ton [108] and 3000 $/ton [38], respectively. The time required to complete one batch of bio-based lactic and succinic acid was assumed to be 3 days [109] and the possibility of market price changes in the future was not considered. The total annual revenue was obtained by multiplying the production of acid per batch by the number of batches per year by the selling price (Table 5-8). On the basis of the estimation of the capital costs, the operating costs, and the revenue, the payback period of each project was shown in Table 5-9.

Table 5-8 Annual revenue estimation

	Annual revenue [M$]
IFBR A	48
IFBR B	49
IFBR C	54
IFBR D	54

Table 5-9 Payback period

	Scenario 1 [year]	Scenario 2 [year]
IFBR A	3.84	3.04
IFBR B	6.05	4.99
IFBR C	8.80	8.84
IFBR D	5.08	5.18

5.2.4 Summary

The results of the economic evaluation indicate that the integrated forest biorefinery (IFBR) between the LA/SA plant and the TMP mill is economically feasible. The IFBRs for LA and SA are profitable and can increase the revenue of the existing TMP mill. The shortest payback period was estimated to be 3 years (IFBR A, scenario2) and 5.1 years (IFBR D, scenario 1) for the production of LA and SA respectively. In the IFBR A, however, the gypsum disposal as a waste by-product makes this conventional method ecologically unattractive. Therefore, it is recommended to develop and implement the IFBR B or the IFBR D, which use the electodialysis as a product recovery method.

CHAPTER 6 GENERAL DISCUSSION

6.1 Process configurations of the stand-alone bio-based LA/SA plants and their simulation models

Five main steps for the production of bio-based lactic and succinic acid from hydrolysate of aspen chips were considered: i) Pretreatment, ii) Enzymatic hydrolysis, iii) Detoxification, iv) Fermentation, v) Product recovery.

Two different configurations depending on the recovery method for each product (lactic and succinic acid) were selected according to several criteria based on high yield, low energy consumption, commercial application, and environmental sustainability:

- Project A: Bio-based lactic acid production with recovery by conventional method (precipitation)
- Project B: Bio-based lactic acid production with recovery by electrodialysis
- Project C: Bio-based succinic acid production with recovery by direct crystallization
- Project D: Bio-based succinic acid production with recovery by electrodialysis

The simulation of the four projects was performed on Aspen Plus, and the material and energy balances from the simulation results match to values from the literature.

6.2 Technical feasibility of the IFBRs

The four configurations were integrated to the TMP process and the following integrated processes were defined:

- IFBR A : Project A + TMP process
- IFBR B : Project B + TMP process
- IFBR C : Project C + TMP process
- IFBR D : Project D + TMP process

The heat recovery opportunities were evaluated by Pinch Analysis. The analysis shows that the concept of an IFBR is technically feasible. LP-steam savings were calculated as 61%, 27%, 20%, and 24% in the IFBR A to D, respectively.

6.3 Economic feasibility of the IFBRs

An economic estimation of each IFBR was performed based on the material balance from the simulation results and the literature review. Individual installed capital costs, operating costs, and revenues by selling LA or SA were estimated and the payback period was calculated. The results show that the concept of an IFBR is economically viable.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

This research was undertaken to demonstrate the technical and economic feasibility of an integrated forest biorefinery consisting of a TMP process and a biorefinery plant for the production of lactic or succinic acid. This study is composed of four parts: the selection of two configurations for the production of lactic and succinic acid, the development of a simulation of the process configurations on Aspen Plus, the integration of the process for the production of lactic or succinic acid into the TMP process, and its economic evaluation.

In the first part of the study, the configurations of the process encompassing a pretreatment, an enzymatic hydrolysis, a detoxification, a fermentation and a recovery step were reviewed. In this project, as almost pure sugars (glucose and xylose) derived from TMP process are supplied for feedstock, the pretreatment and the detoxification are not considered. Two different configurations of the process for each product (lactic and succinic acid) were developed taking into account the recovery process: the production of bio-biased lactic acid with recovery by conventional method (precipitation) and electrodialysis, and the production of bio-based succinic acid with recovery by direct crystallization and electrodialysis.

In the next step, a simulation on Aspen Plus for both the stand-alone bio-based lactic and succinic acid plants was performed. The material and energy balances were calculated based on the results of the simulation.

The integration of the process for both the stand-alone bio-based lactic and succinic acid plants to the TMP process was done. A pinch analysis was carried out for each process and the pinch point, the total energy requirement and the energy level to be provided were determined from the Composite Curves and the Grand Composite Curve. The Heat Exchanger Network of the four integrated forest biorefineries was designed and the heat recovery opportunity was estimated. From the results of the process integration, the reduction in hot utility (LP-steam) is possible, as compared to a stand-alone biorefinery plant for the production of lactic or succinic acid.

At the end of the project, an economic evaluation based on the material balance and the energy use in the integrated processes was also performed. The capital costs, the annual operating costs, the annual revenues, and the payback period of the four integrated forest biorefineries were estimated.

In conclusion, it was shown that the integrated forest biorefinery (IFBR) based on a bio-based LA/SA plant and a TMP mill is feasible technically and economically. The concept of IFBR can be a practicable alternative not only for the economically sustainable operation of the existing TMP mill but also for the production of bio-based chemicals. In the economic view, lactic acid production with recovery by conventional method (precipitation, IFBR A) is proposed, however, it creates gypsum disposal. In the environmental view, lactic and succinic acid production with recovery by electrodialysis (IFBR B and D) are proposed. Among these two integrated biorefinery, the former option might be recommended, since there is already a bio-succinic acid manufacture (BioAmber) in Ontario, Canada.

7.2 Recommendations

The following recommendations have been formulated for future studies:

- The simulation of the process configuration for the production of bio-based lactic and succinic acid from the pretreatment of wood, including the detoxification, should be developed to generalize the application of the simulation.
- Additional combinations of HEX designs should be proposed to diversify the strategies for their optimization.
- Process integration options considering water and chemicals consumptions should be evaluated.

BIBLIOGRAPHY

[1] U. S. E. I. Administration. (2014). *overview data for Canada*. Available: http://www.eia.gov/countries/country-data.cfm?fips=CA#pet

[2] T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, *et al.*, "Top Value Added Chemicals from Biomass," US department of energy2004.

[3] C. Å kerberg and G. Zacchi, "An economic evaluation of the fermentative production of lactic acid from wheat flour," *Bioresource Technology*, vol. 75, pp. 119-126, 2000.

[4] N. R. Canada. (2014). *Biomass, bioenergy and bioproducts*. Available: http://www.nrcan.gc.ca/forests/industry/13315

[5] Douglas Bradley, "IEA Bioenergy Task 40 Country Report Canada 2011 " 2012.

[6] R. C. Pettersen, "The chemical composition of wood," *The chemistry of solid wood*, vol. 207, pp. 57-126, 1984.

[7] H. Per and A. J. Mark, "Structure and Degradation Process for Waterlogged Archaeological Wood," in *Archaeological Wood*, ed: American Chemical Society, 1989, pp. 35-65.

[8] P. Kumar, D. M. Barrett, M. J. Delwiche, and P. Stroeve, "Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 3713-3729, 2009.

[9] UNIFOR, "Economic and Financial Overview of the Eastern Canada Pulp and Paper Industry," in *UNIFOR WAGE POLICY CONFERENCE*, Montreal, 2014.

[10] Lydia Couture and Ryan Macdonald, "The Great U.S. Recession and Canadian Forest Products," in *Economic insights* vol. 28, ed: Statistics Canada, 2013.

[11] N. R. Canada. Canada's forest industry by the numbers [Online]. Available: http://www.nrcan.gc.ca/forests/industry/13311

[12] GREG KEENAN, DAVID PARKINSON, and BRENT JANG. (2014). *Paper trail: The decline of Canada's forestry industry*. Available: http://www.theglobeandmail.com/report-on-business/economy/paper-trail-the-fall-of-forestry/article21967746/

[13] N. R. Canada. (2009). *Pulp and Paper Green Transformation Program: Mission accomplished*. Available: http://www.nrcan.gc.ca/forests/federal-programs/13141

[14] N. R. Canada. (2014). *Statistical data - Domestic economic impact (Canada)*. Available: http://cfs.nrcan.gc.ca/statsprofile/economicimpact/ca

[15] G.A. SMOOK, *HANDBOOK FOR PULP & PAPER TECHNOLOGISTS*, 1934.

[16] C. J. Biermann and C. Biermann, *Handbook of pulping and papermaking* vol. 2: Academic press, 1996.

[17] L. Christopher, *Integrated forest biorefineries*: Royal Society of Chemistry, 2012.

[18] Heather Dewar and François Soulard, "Human Activity and the Environment - Freshwater supply and demand in Canada," E. A. a. S. Division, Ed., ed. Ottawa: authority of the Minister responsible for Statistics Canada, 2010.

[19] N. R. Canada, "BENCHMARKING ENERGY USE IN CANADIAN PULP AND PAPER MILLS," Nature Resources Canada2008.

[20] B. Kamm, *Biorefineries - Industrial Processes and Products*: WILEY, 2010.

[21] I. Bioenergy, "Biorefineries: adding value to the sustainable utilisation of biomass," 2009.

[22] F. Cherubini, G. Jungmeier, M. Wellisch, T. Willke, I. Skiadas, R. Van Ree, *et al.*, "Toward a common classification approach for biorefinery systems," *Biofuels, Bioproducts and Biorefining*, vol. 3, pp. 534-546, 2009.

[23] NRCan, "STRATEGIC PLAN 2020," 2014.

[24] S.N. Naik, Vaibhav V. Goud, Prasant K. Rout, and Ajay K. Dalai, "Production of first and second generation biofuels: A comprehensive review," *Renewable and Sustainable Energy Reviews*, vol. 14, pp. 578-597, 2010.

[25] Giuliano Dragone, Bruno Fernandes, António A. Vicente, and José A. Teixeira, *Third generation biofuels from microalgae* Spain: Formatex Research Center, 2010.

[26] Y. Lin and S. Tanaka, "Ethanol fermentation from biomass resources: current state and prospects," *Applied Microbiology and Biotechnology*, vol. 69, pp. 627-642, 2006/02/01 2006.

[27] Wei Zhang and A. Geng., "Improved ethanol production by a xylose fermenting recombinant yeast strain constructed through a modified genome shuffling method," *Biotechnology for Biofuels*, vol. 5, 2012.

[28] H. Benninga, *A History of Lactic Acid Making*. Dordrecht, Netherlands: Springer Netherlands, 1990.

[29] Y. Tashiro, W. Kaneko, Y. Sun, K. Shibata, K. Inokuma, T. Zendo, *et al.*, "Continuous d-lactic acid production by a novelthermotolerant Lactobacillus delbrueckii subsp. lactis QU 41," *Applied Microbiology and Biotechnology*, vol. 89, pp. 1741-1750, 2011.

[30] Y. Wang, Y. Tashiro, and K. Sonomoto, "Fermentative production of lactic acid from renewable materials: Recent achievements, prospects, and limits," *Journal of Bioscience and Bioengineering*, 2014.

[31] G. V. Research, "Lactic Acid And Poly Lactic Acid (PLA) Market Analysis By Application (Packaging, Agriculture, Transport, Electronics, Textiles) And Segment Forecasts To 2020," Grand View Research, Inc. 2014.

[32] Y. Li and F. Cui, "Microbial Lactic Acid Production from Renewable Resources," pp. 211-228, 2010.

[33] Y.-J. W. Wee, J.-N. K. Kim, and H.-W. R. Ryu, "Biotechnological Production of Lactic Acid and Its Recent Applications," *Biotechnological Production of Lactic Acid, Food Technol.*, vol. 44, pp. 163-172, 2006.

[34] M. A. Abdel-Rahman, Y. Tashiro, and K. Sonomoto, "Recent advances in lactic acid production by microbial fermentation processes," *Biotechnol Adv*, vol. 31, pp. 877-902, Nov 2013.

[35] J. Sadhukhan, K. S. Ng, and E. M. Hernandez, *Biorefineries and Chemical Processes : Design, Integration and Sustainability Analysis*. Somerset, NJ, USA: Wiley, 2014.

[36] J. Akhtar, A. Idris, and R. Abd Aziz, "Recent advances in production of succinic acid from lignocellulosic biomass," *Appl Microbiol Biotechnol,* vol. 98, pp. 987-1000, Feb 2014.

[37] H. Song and S. Y. Lee, "Production of succinic acid by bacterial fermentation," *Enzyme and Microbial Technology,* vol. 39, pp. 352-361, 2006.

[38] s. r. o. WEASTRA, "WP 8.1. Determination of market potential for selected platform chemicals (Itaconic acid, Succinic acid, 2,5-Furandicarboxylic acid)," 2012.

[39] A. T. W. M. Hendriks and G. Zeeman, "Pretreatments to enhance the digestibility of lignocellulosic biomass," *Bioresource Technology,* vol. 100, pp. 10-18, 2009.

[40] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple, *et al.*, "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresource Technology,* vol. 96, pp. 673-686, 4// 2005.

[41] P.F.H. Harmsen, W.J.J. Huijgen, L.M. Bermúdez López, and R.R.C. Bakker, "Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass " Energy Research Centre of the Netherlands2010.

[42] G. Brodeur, E. Yau, K. Badal, J. Collier, K. B. Ramachandran, and S. Ramakrishnan, "Chemical and Physicochemical Pretreatment of Lignocellulosic Biomass: A Review," *Enzyme Research,* vol. 2011, p. 17, 2011.

[43] A. A. Modenbach and S. E. Nokes, "Enzymatic hydrolysis of biomass at high-solids loadings – A review," *Biomass and Bioenergy,* vol. 56, pp. 526-544, 9// 2013.

[44] M. Zhang, R. Su, W. Qi, and Z. He, "Enhanced Enzymatic Hydrolysis of Lignocellulose by Optimizing Enzyme Complexes," *Applied Biochemistry and Biotechnology,* vol. 160, pp. 1407-1414, 2010/03/01 2010.

[45] B. Alriksson, A. Cavka, and L. J. Jonsson, "Improving the fermentability of enzymatic hydrolysates of lignocellulose through chemical in-situ detoxification with reducing agents," *Bioresour Technol,* vol. 102, pp. 1254-1263, 2011.

[46] E. Palmqvist and B. Hahn-Hägerdal, "Fermentation of lignocellulosic hydrolysates. I: inhibition and detoxification," *Bioresource Technology,* vol. 74, pp. 17-24, 8// 2000.

[47] C. Luo, D. L. Brink, and H. W. Blanch, "Identification of potential fermentation inhibitors in conversion of hybrid poplar hydrolyzate to ethanol," *Biomass and Bioenergy,* vol. 22, pp. 125-138, 2// 2002.

[48] P.S. Bryant, E.W. Malcolm, and C.P. Woitkovich, "Pulp and Paper Mill Water Use in North America," presented at the TAPPI Environmental Conference Exhibit, Orlando, Florida, 1996.

[49] R. Mala and A. Ramakrishnan, "Bioethanol from Lignocellulosic Biomass Part III Hydrolysis and Fermentation," in *Handbook of Plant-Based Biofuels*, ed: CRC Press, 2008, pp. 159-173.

[50] J. C. Parajó, H. Dominguez, and J. M. Domínguez, "Improved xylitol production with Debaryomyces hansenii Y-7426 from raw or detoxified wood hydrolysates," *Enzyme and Microbial Technology,* vol. 21, pp. 18-24, 7// 1997.

[51] N.-O. Nilvebrant, A. Reimann, S. Larsson, and L. Jönsson, "Detoxification of lignocellulose hydrolysates with ion-exchange resins," *Applied Biochemistry and Biotechnology,* vol. 91-93, pp. 35-49, 2001/03/01 2001.

[52] JJ Fenske, DA Griffin, and MH Penner, "Comparison of aromatic monomers in lignocellulosic biomass prehydrolysates," *Journal of Industrial Microbiology & Biotechnology,* vol. 20, pp. 364-368, 1998.

[53] M. J. López, N. N. Nichols, B. S. Dien, J. Moreno, and R. J. Bothast, "Isolation of microorganisms for biological detoxification of lignocellulosic hydrolysates," *Applied Microbiology and Biotechnology,* vol. 64, pp. 125-131, 2004/03/01 2004.

[54] M. A. Abdel-Rahman, Y. Tashiro, and K. Sonomoto, "Lactic acid production from lignocellulose-derived sugars using lactic acid bacteria: Overview and limits," *Journal of Biotechnology,* vol. 156, pp. 286-301, 2011.

[55] A. Aden, M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, *et al.*, "Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover," Netional Renewable Energy Laboratory2002.

[56] L. I. G-Alegría E, Ruiz JI, Sáenz J, Fernández E, Zarazaga M, Dizy M, Torres C, Ruiz-Larrea F., "High tolerance of wild Lactobacillus plantarum and Oenococcus oeni strains to lyophilisation and stress environmental conditions of acid pH and ethanol," *FEMS Microbiology Letters,* vol. 230, pp. 53-61, 2004.

[57] J.-E. G. Luciane Lapierre, Andreas Ott, Michele Delley, Beat Mollet,, "D-Lactate Dehydrogenase Gene (ldhD) Inactivation and Resulting Metabolic Effects in the Lactobacillus johnsonii Strains La1 and N312," *Applied Environmenal Microbiology,* vol. 81, pp. 4002-4007, 1999.

[58] J. G. Zeikus, M. K. Jain, and P. Elankovan, "Biotechnology of succinic acid production and markets for derived industrial products," *Applied Microbiology and Biotechnology,* vol. 51, pp. 545-552, 1999/05/01 1999.

[59] M. G. Adsul, M. S. Singhvi, S. A. Gaikaiwari, and D. V. Gokhale, "Development of biocatalysts for production of commodity chemicals from lignocellulosic biomass," *Bioresource Technology,* vol. 102, pp. 4304-4312, 2011.

[60] K. Jantama, M. J. Haupt, S. A. Svoronos, X. Zhang, J. C. Moore, K. T. Shanmugam, *et al.*, "Combining metabolic engineering and metabolic evolution to develop nonrecombinant strains of Escherichia coli C that produce succinate and malate," *Biotechnology and Bioengineering,* vol. 99, pp. 1140-1153, 2008.

[61] H. Song, J. W. Lee, S. Choi, J. K. You, W. H. Hong, and S. Y. Lee, "Effects of dissolved CO2 levels on the growth of Mannheimia succiniciproducens and succinic acid production," *Biotechnology and Bioengineering,* vol. 98, pp. 1296-1304, 2007.

[62] P. C. Lee, W. G. Lee, S. Kwon, S. Y. Lee, and H. N. Chang, "Succinic acid production by Anaerobiospirillum succiniciproducens: effects of the H2/CO2 supply and glucose concentration," *Enzyme and Microbial Technology,* vol. 24, pp. 549-554, 6/1/ 1999.

[63] M. V. Guettler, D. Rumler, and M. K. Jain, "Actinobacillus succinogenes sp. nov., a novel succinic-acid-producing strain from the bovine rumen," *International Journal of Systematic Bacteriology,* vol. 49, pp. 207-216, 1999.

[64] M. V. Guettler, M. K. Jain, and D. Rumler, "Method for making succinic acid, bacterial variants for use in the process, and methods for obtaining variants," US Patent, 1996.

[65] N. S. Samuelov, R. Datta, M. K. Jain, and J. G. Zeikus, "Whey Fermentation by Anaerobiospirillum succiniciproducens for Production of a Succinate-Based Animal Feed Additive," *Applied and Environmental Microbiology,* vol. 65, pp. 2260-2263, 1999.

[66] P. C. Lee, S. Y. Lee, S. H. Hong, H. N. Chang, and S. C. Park, "Biological conversion of wood hydrolysate to succinic acid by Anaerobiospirillum succiniciproducens," *Biotechnology Letters,* vol. 25, pp. 111-114, 2003.

[67] R. Datta, "PROCESS FOR THE PRODUCTION OF SUCCINIC ACID BY ANAEROBIC FERMENTATION," 5143833 A, 1992.

[68] G. C. Inskeep, G. G. Taylor, and W. C. Breitzke, "LACTIC ACID FROM CORN SUGAR," *Industrial & Engineering Chemistry,* vol. 44, pp. 1955-1966, 1952.

[69] J. Vijayakumar, R. Aravindan, and T. Viruthagiric, "Recent Trends in the Production, Purification and Application of Lactic Acid," *Chem. Biochem. Eng. Q.,* vol. 22, pp. 245-264, 2008.

[70] R. Datta and M. Henry, "Lactic acid: recent advances in products, processes and technologies — a review," *Journal of Chemical Technology & Biotechnology,* vol. 81, pp. 1119-1129, 2006.

[71] K. L. WASEWAR, "Separationof Lactic Acid:RecentAdvances," *Chem. Biochem. Eng. Q.,* vol. 19, pp. 159-172, 2005.

[72] Y. Li, A. Shahbazi, K. Williams, and C. Wan, "Separate and Concentrate Lactic Acid Using Combination of Nanofiltration and Reverse Osmosis Membranes," *Applied Biochemistry and Biotechnology,* vol. 147, pp. 1-9, 2008/03/01 2008.

[73] N. Boniardi, R. Rota, G. Nano, and B. Mazza, "Lactic acid production by electrodialysis Part I: Experimental tests," *Journal of Applied Electrochemistry,* vol. 27, pp. 125-133, 1997.

[74] E. G. Lee, S.-H. Moon, Y. Keun Chang, I.-K. Yoo, and H. Nam Chang, "Lactic acid recovery using two-stage electrodialysis and its modelling," *Journal of Membrane Science,* vol. 145, pp. 53-66, 6/24/ 1998.

[75] Shri Ramaswamy, Hua-Jiang Huang, and Bandaru V. Ramarao, *Separation and Purification Technologies in Biorefineries*. Somerset, NJ, USA: John Wiley & Sons, 2013.

[76] T. Franken, "Bipolar membrane technology and its applications," *Membrane Technology,* vol. 2000, pp. 8-11, 9// 2000.

[77] Y. H. Kim and S.-H. Moon, "Lactic acid recovery from fermentation broth using one-stage electrodialysis," *Journal of Chemical Technology & Biotechnology,* vol. 76, pp. 169-178, 2001.

[78] M. V. Guettler, M. K. Jain, and B. K. Soni, "Process for making succinic acid, microorganisms for use in the process and methods of obtaining the microorganisms," 5723322, 1998.

[79] B. Kim, Y. Hong, and W. Hong, "Effect of salts on the extraction characteristics of succinic acid by predispersed solvent extraction," *Biotechnology and Bioprocess Engineering,* vol. 9, pp. 207-211, 2004.

[80] R. Luque, C. S. K. Lin, C. Du, D. J. Macquarrie, A. Koutinas, R. Wang, *et al.*, "Chemical transformations of succinic acid recovered from fermentation broths by a novel direct vacuum distillation-crystallisation method," *Green Chemistry,* vol. 11, pp. 193-200, 2009.

[81] I. Meynial-Salles, S. Dorotyn, and P. Soucaille, "A new process for the continuous production of succinic acid from glucose at high yield, titer, and productivity," *Biotechnology and Bioengineering,* vol. 99, pp. 129-135, 2008.

[82] Q. Li, D. Wang, Y. Wu, W. Li, Y. Zhang, J. Xing, *et al.*, "One step recovery of succinic acid from fermentation broths by crystallization," *Separation and Purification Technology,* vol. 72, pp. 294-300, 2010.

[83] T. Kurzrock and D. Weuster-Botz, "Recovery of succinic acid from fermentation broth," *Biotechnology Letters,* vol. 32, pp. 331-339, 2010.

[84] B. LINNHOFF, TOWNSEND, D. W., BOLAND, D., HEWITT, G. F., THOMAS, B. E. A., GUY, A. R., *A user guide on process integration for the efficient use of energy* 2nd ed. Rugby, UK: Institution of Chemical Engineers, 1994a.

[85] N. R. Canada, "Pinch Analysis: For the Efficient Use of Energy, Water & Hydrogen," 2003.

[86] Ian C. Kemp, *Pinch Analysis and Process Integratoin*. Oxford UK: Elsevier, 2007.

[87] D.W. Francis, M.T. Towers, and T.C. Browne, "Energy Cost Reduction in the Pulp and Paper Industry – An Energy Benchmarking Perspective," Paprican 2002.

[88] N. Martin, N. Anglani, D. Einstein, M. Khrushch, E. Worrell, and L.K. Price, "Opportunities to Improve Energy Efficiency and Reduce Greenhouse Gas Emissions in the U.S. Pulp and Paper Industry," ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY2000.

[89] S. Lafourcade, J. Labidi, R. Koteles, C. Gélinas, and P. Stuart, "Thermal pinch analyses with process steam mixing at a TMP-newsprint mill. ," *Pulp and Paper Canada,* vol. 104, pp. 74-77, 2003.

[90] J. JACOB, H. KAIPE, F. COUDERC, and J. PARIS, "WATER NETWORK ANALYSIS IN PULP AND PAPER PROCESSES BY PINCH AND LINEAR PROGRAMMING TECHNIQUES," *Chem. Eng. Comm.*, vol. 189, pp. 184-206, 2002.

[91] E. Mateos-Espejel, M. Marinova, S. Bararpour, and J. Paris, "Energy Implications of Water Reduction Strategies in Kraft Process. Part I: Methodology," *Pulp & Paper Canada,* vol. May/June, pp. 34-37, 2010.

[92] E. Mateos-Espejel, M. Marinova, S. Bararpour, and J. Paris, "Energy Implications of Water Reduction Strategies in Kraft Process. Part II: Results," *Pulp & Paper Canada,* vol. May/June, pp. 38-41, 2010.

[93] R. K. William, J. H. Carl, L. Jose, W. J. Thomas, and G. H. Eric, "Pretreatments for Converting Wood into Paper and Chemicals," in *Materials, Chemicals, and Energy from Forest Biomass*. vol. 954, ed: American Chemical Society, 2007, pp. 392-408.

[94] S. C. Eric D. Larson, Ryan E. Katofsky, Kristiina Lisa, W. James Frederick Jr., "An Assessment of Gasification-Based Biorefining at Kraft Pulp and Paper Mills in the United States, Part A: Background and Assumptions," *TAPPI*, vol. 7, pp. 8-14, 2008.

[95] A. v. Heiningen, "Converting a kraft pulp mill into an integrated forest biorefinery," *PULP & PAPER CANADA*, vol. 107, pp. 141-146, 2006.

[96] G. o. Canada. (2010). *Trada data online*. Available: https://www.ic.gc.ca/app/scr/tdst/tdo/crtr.html?currency=CDN&toFromCountry=CDN&searchType=BL&hSelectedCodes=%7c322111&productType=NAICS&grouped=GROUPED&reportType=DS&timePeriod=5%7cComplete+Years&changeCriteria=true

[97] H.-J. Huang, W. Lin, S. Ramaswamy, and U. Tschirner, "Process Modeling of Comprehensive Integrated Forest Biorefinery—An Integrated Approach," *Applied Biochemistry and Biotechnology*, vol. 154, pp. 26-37, 2009.

[98] C. Mao, Z. Yuan, D. Wong, W. W. A. Dajani, and T. Browne, "FPInnovations' novel fractionation process for lignocellulosic biomass," presented at the Nordic Wood Biorefinery Conference, Helsinki, Finland, 2012.

[99] A. B. Moldes, A. Torrado, A. Converti, and J. M. Domínguez, "Complete bioconversion of hemicellulosic sugars from agricultural residues into lactic acid by Lactobacillus pentosus," *Applied Biochemistry and Biotechnology*, vol. 135, pp. 219-227, 2006.

[100] S. C. Pan, W. H. Peterson, and M. J. Johnson, "Acceleration of Lactic Acid Fermentation by Heat–Labile Substances," *Industrial & Engineering Chemistry*, vol. 32, pp. 709-714, 1940.

[101] D. Y. Kim, S. C. Yim, P. C. Lee, W. G. Lee, S. Y. Lee, and H. N. Chang, "Batch and continuous fermentation of succinic acid from wood hydrolysate by Mannheimia succiniciproducens MBEL55E," *Enzyme and Microbial Technology*, vol. 35, pp. 648-653, 12/1/ 2004.

[102] Y.-P. Liu, P. Zheng, Z.-H. Sun, Y. Ni, J.-J. Dong, and P. Wei, "Strategies of pH control and glucose-fed batch fermentation for production of succinic acid by Actinobacillus succinogenes CGMCC1593," *Journal of Chemical Technology & Biotechnology*, vol. 83, pp. 722-729, 2008.

[103] A. Vlysidis, M. Binns, C. Webb, and C. Theodoropoulos, "A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals," *Energy*, vol. 36, pp. 4671-4683, 2011.

[104] B. o. L. Statistics. (1980-2012). *Employment, Hours, and Earnings from the Current Employment Statistics survey (National)* Available: http://www.bls.gov/data/

[105] K. P. Rickard Fornell, Thore Berntsson,, "Energy efficiency measures in a kraft pulp mill converted to a biorefinery producing ethanol and DME from Softwood," *CHEMICAL ENGINEERING TRANSACTIONS* vol. 21, pp. 1147-1152, 2010.

[106] C. E. Association. (2014). *Key Canadian Electricity Statistics*. Available: http://www.electricity.ca/media/Electricity101/KeyCanadianElectricityStatistics10June2014.pdf

[107] Methanex. (2015). *methanol prices for North America, Europe and Asia*. Available: https://www.methanex.com/our-business/pricing

[108] cellulac. *MARKET*. Available: http://cellulac.co.uk/en/market/

[109] P. S. Panesar, J. F. Kennedy, C. J. Knill, and M. Kosseva, "Production of L(+) lactic acid using Lactobacillus casei from whey," *Brazilian Archives of Biology and Technology,* vol. 53, pp. 219-226, 2010.

[110] R. Smith, *Chemical Process Design and Integration*. England: WILEY, 2005.

[111] P. Fraas, *Heat Exchanger Design*: WILEY, 1989.

APPENDIX A – REACTIONS IN THE ASPEN PLUS SIMULATION

Table A1 Reactions assumed to occur in the enzymatic hydrolysis

Enzymatic hydrolysis (50 ℃, 1 atm)	
CELLULOS + H2O → GLUCOSE	0.6
XYLAN + H2O → XYLOSE	0.7
ACETATE → ACETIC ACID	0.28
GALACTAN → GALAOLIG	0.3
CELLULOS → GLUCOLIG	0.05
XYLAN → XYLOLIG	0.05

Table A2 Reactions assumed to occur in the fermentation of lactic acid

Fermentation (45 ℃, 1 atm)	
GLUCOSE → 2 LACID	0.85
3 XYLOSE → 5 LACID	0.8

Table A3 Reactions assumed to occur in the recovery of lactic acid with conventional method

Precipitation	
H2SO4 + CA(OH)2 → GYPSUM	1
Esterification (70 ℃, 1 atm)	
LACID + METHANOL → METHYL LACTATE + H2O	1
Hydrolysis (100 ℃, 1 atm)	
METHYL LACTATE + H2O → LACID + METHANOL	1

Table A4 Reactions assumed to occur in the fermentation of succinic acid

Fermentation (37 ℃, 1 atm)	
7 GLUCOSE + 2 CO2 → 12 SUCCACID + 6 H2O	0.75
7 XYLOSE + 5 CO2 → 10 SUCCACID + 6 H2O	0.43

APPENDIX B – STREAM DATA FOR THE ENERGY ANALYSIS

Table B1 Stream data for the TMP mill

No.	Type	Stream	T_{in} [°C]	T_{out} [°C]	Heat load [kW]
1	Cold	Line 1_Water heating	69.87	70.00	96.70
2	Cold	Clear filtrate from PM	58.98	83.00	7973.02
3	Cold	Demin water_reboiler	124.00	141.75	59116.28
4	Cold	Filtrate PM	58.98	65.24	3585.50
5	Cold	Water_Line 1 make up	25.00	56.27	5798.68
6	Cold	Water Line 3_make up	14.00	70.00	8382.40
7	Cold	Water PM_make up (1)	14.00	55.00	13779.75
8	Cold	Water PM_make up (2)	28.50	55.00	1762.79
9	Cold	Water PM_make up (3)	35.00	55.00	2826.54
10	Cold	Water PM_make up (4)	14.00	20.96	144.67
11	Cold	Air input_PM	4.00	34.00	3936.34
12	Cold	Water PM_make up (5)	18.00	60.00	1438.20
13	Cold	Filtrate heating Wire pit	64.46	70.54	2503.60
14	Cold	LP Steam Dryer	138.90	167.00	44813.32
15	Cold	LP Line 3	138.90	167.00	3459.20
16	Cold	MP Line 1	138.90	219.00	889.41
17	Cold	Demin water deareator	14.00	124.00	3817.91
18	Cold	Denaturing	50.00	90.00	6631.44
19	Cold	Other steam needs	138.00	167.00	11860.00
20	Cold	Water heating	4.00	55.00	13900.00
21	Hot	Line 3_Effluent_a	90.52	30.00	12112.71
22	Hot	Line 3_Effluent_b	99.49	30.00	4463.71
23	Hot	Line 1_Effluent	87.99	30.00	4891.53
24	Hot	Rejects refiners Dirty steam	131.17	126.15	8055.59
25	Hot	Effluent	87.99	30.00	4891.53
26	Hot	Line 3_Dirty steam	149.27	135.01	32963.06
27	Hot	Line 1_Dirty steam	147.06	147.06	26159.78
28	Hot	Cloudy Line 1	69.31	56.27	8369.05
29	Hot	Filtrate Line 1	64.46	56.27	1014.67
30	Hot	Air exhaust PM	96.50	28.45	21274.46
31	Hot	Water recycle	55.00	23.09	1155.97
32	Hot	Condensate return deareator	138.90	124.00	1298.71
33	Hot	Effluent_bio	55.00	30.00	9658.55
34	Hot	Dirty steam	163.80	163.70	13351.80
35	Hot	Dirty condensate	163.70	30.00	4299.84

Table B2 Stream data for the stand alone bio-base lactic acid plant with the recovery by precipitation

No.	Type	Stream	T_{in} [℃]	T_{out} [℃]	Heat load [kW]
1	Cold	Methanol_esterification reactor	20.00	100.00	6461.13
2	Cold	Water_gypsum filtration	4.00	70.00	13024.00
3	Cold	Water_filtration after enzymatic hydrolysis	4.00	50.00	8908.89
4	Cold	Water_filtration after fermentation	4.00	45.00	7905.05
5	Cold	Water_hydrolysis reactor	20.00	100.00	2594.96
6	Cold	Water_enzymatic hydrolysis reactor	4.00	50.00	3299.59
7	Cold	Sulfuric acid_precipitation reactor	20.00	70.00	489.01
8	Cold	Lactic acid_heating to evaporation	69.47	101.00	89685.60
9	Cold	Lactic acid_heating to precipitation	45.00	70.00	4634.45
10	Cold	Methylactate_Distillation #1	100.28	100.81	84270.63
11	Cold	Lactic acid_Distillation #2	100.32	101.67	58413.96
12	Cold	Hydrolysis	100.00	100.50	6540.33
13	Cold	Esterification	92.09	100.00	20869.65
14	Cold	Enzymatic hydrolysis	50.00	50.50	156.34
15	Hot	Lactic acid_cooling	101.00	30.00	1820.37
16	Hot	Methanol_Distillation #1	97.83	90.15	78068.62
17	Hot	Methanol_Distillation #2	100.07	98.62	56358.14
18	Hot	Fermentation	47.83	45.00	1830.45
19	Hot	Evaporation	101.67	101.00	18.54

Table B3 Stream data for the stand alone bio-base lactic acid plant with the recovery by electrodialysis

No.	Type	Stream	T_{in} [℃]	T_{out} [℃]	Heat load [kW]
1	Cold	Methanol_esterification reactor	20.00	100.00	6461.13
2	Hot	Lactic acid_cooling	101.00	30.00	2557.09
3	Cold	Water_filtration after enaymztic hydrolysis	4.00	50.00	8908.89
4	Cold	Water_filtration after fermentation	4.00	45.00	7905.05
5	Cold	Water_hydrolysis reactor	20.00	100.00	2594.96
6	Cold	Water_enzymatic hydrolysis reactor	20.00	50.00	2180.99
7	Cold	Lactic acid_heating to evaporation	45.00	101.00	142474.86
8	Cold	Methylactate_Distillation #1	100.32	100.81	84270.63
9	Hot	Methanol_Distillation #1	97.74	90.21	71529.42
10	Cold	Lactic acid_Distillation #2	100.37	101.46	56283.17
11	Hot	Methanol_Distillation #2	100.05	98.25	53915.98
12	Hot	Fermentation	48.74	45.00	1950.49
13	Cold	Hydrolysis	100.00	100.50	8489.17
14	Cold	Esterification	92.29	100.00	25591.28
15	Hot	Evaporation	101.46	101.00	17.83
16	Cold	Enzymatic hydrolysis	50.00	50.50	156.34

Table B4 Stream data for the stand alone bio-base succinic acid plant with the recovery by direct crystallization

No.	Type	Stream	T_{in} [℃]	T_{out} [℃]	Heat load [kW]
1	Cold	Air_heating to dryer	4.00	100.00	962.79
2	Cold	Water_filtration after enaymztic hydrolysis	4.00	50.00	8908.89
3	Cold	Water_filtration after fermentation	4.00	37.00	6318.25
4	Cold	Water_enzymatic hydrolysis reactor	4.00	50.00	3299.59
5	Cold	Succinic acid_heating to evaporation	37.00	102.00	290319.93
6	Cold	Evaporation	102.00	102.50	1596.30
7	Cold	Enzymatic hydrolysis	50.00	50.50	614.41
8	Hot	Sugars_cooling to fermentation	50.00	37.00	3577.55
9	Hot	Succinic acid_cooling to crystallization	102.00	4.00	1904.31
10	Hot	Air_cooling from dryer	64.27	4.00	5723.80
11	Hot	Fermentation	37.44	37.00	2516.96

Table B5 Stream data for the stand alone bio-base succinic acid plant with the recovery by direct crystallization

No.	Type	Stream	T_{in} [℃]	T_{out} [℃]	Heat load [kW]
1	Cold	Air_heating to dryer	4.00	100.00	962.79
2	Cold	Water_filtration after enaymztic hydrolysis	4.00	50.00	8908.89
3	Cold	Water_filtration after fermentation	4.00	37.00	6318.25
4	Cold	Water_enzymatic hydrolysis reactor	4.00	50.00	3299.59
5	Cold	Succinic acid_heating to evaporation	37.00	102.00	234163.89
6	Cold	Evaporation	102.00	102.50	957.83
7	Cold	Enzymatic hydrolysis	50.00	50.50	156.34
8	Hot	Air_cooling from dryer	69.71	4.00	5763.93
9	Hot	Sugars_cooling to fermentation	50.00	37.00	3577.55
10	Hot	Succinic acid_cooling to crystallization	102.00	4.00	1142.25
11	Hot	Fermentation	37.44	37.00	2516.96

APPENDIX C – HEAT EXCHANGER NETWORK OF IFBRS

Table C 1 Integrated bio-based lactic acid plant with the recovery by precipitation in scenario 1 (IFBR A, Scenario 1)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-126	Reboiler (distillation #2)	100.32	100.32	Line 3_Dirty steam	135.07	135.01	0.12	33.85
E-115	Esterification	92.09	100.00	LP-STEAM	163.31	149.02	10.49	1755.24
E-117	Esterification	92.09	100.00	Dirty condensate	107.38	97.90	0.30	583.36
E-111	Methanol supply to the esterification	75.62	100.00	Dirty condensate	163.70	160.57	0.10	13.67
E-124	Methanol supply to the esterification	20.00	75.62	Dirty condensate	82.69	30.00	0.23	341.90
E-112	Crude LA produced from the precipitation, sent to the evaporation	97.97	101.00	LP-STEAM	167.00	163.31	9.28	1413.58
E-114	Reboiler (distillation #2)	100.32	101.67	LP-STEAM	163.31	149.02	25.45	4639.39
E-116	Reboiler (distillation #2)	100.32	101.67	Line 3_Dirty steam	149.27	135.07	32.85	8058.99
E-122	Enzymatic Hydrolysis	50.00	50.50	LP-STEAM	149.02	110.00	0.16	20.14
E-113	Crude LA produced from the precipitation, sent to the evaporation	97.97	101.00	Dirty condensate	160.57	107.38	1.71	655.38
E-119	H2SO4 supply to the precipitation	20.00	70.00	Dirty condensate	97.90	82.69	0.49	123.10
E-123	Methanol supply to the esterification	96.01	97.97	LP-STEAM	149.02	110.00	7.07	2511.95
E-121	Reboiler (distillation #1)	100.28	100.81	LP-STEAM	149.02	110.00	84.27	35303.02
E-118	water supply to the hydrolysis of methylactate	74.24	100.00	LP-STEAM	149.02	110.00	0.10	27.43
E-120	Hydrolysis	100.00	100.50	LP-STEAM	149.02	110.00	6.54	2698.41
Sum							179.15	58179.41

Table C 2 Integrated bio-based lactic acid plant with the recovery by precipitation in scenario 2 (IFBR A, Scenario 2)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-142	water supply to the hydrolysis of methylactate	20.90	74.24	Condenser (distillation #1)	93.56	93.33	1.73	9.01
E-144	Reboiler (distillation #1)	100.28	100.81	Line 3_Dirty steam	139.35	135.07	9.91	2706.85
E-148	H2SO4 supply to the precipitation	20.00	70.00	LP-STEAM	113.75	110.00	0.49	51.04
E-146	water supply to the hydrolysis of methylactate	20.00	20.90	LA cooling	44.13	42.93	0.03	0.53
E-150	Enzymatic Hydrolysis	50.00	50.50	LP-STEAM	113.75	110.00	0.16	25.38
E-133	crude LA produced from the precipitation, sent to the evaporation	85.66	96.65	Condenser (distillation #2)	100.07	98.83	36.82	1710.49
E-135	water supply to enzymatic hydrolysis	4.00	20.00	Fermentation	47.83	45.00	1.15	180.21
E-119	water supply to filtration after fermentation	5.21	45.00	Condenser (distillation #1)	97.83	96.45	7.67	55.85
E-121	water supply to filtration after enzymatic hydrolysis	20.76	50.00	Condenser (distillation #1)	97.83	96.45	4.42	36.92
E-143	water supply to filtration after enzymatic hydrolysis	5.63	17.24	Dirty condensate	99.91	30.00	2.25	267.94
E-141	crude LA produced from the precipitation, sent to the evaporation	77.56	85.66	Condenser (distillation #2)	98.83	98.62	2.60	22.78
E-138	water supply to the hydrolysis of methylactate	74.24	96.83	LP-STEAM	143.11	143.11	0.00	0.05
E-126	Esterification	95.91	100.00	Line 3_Dirty steam	149.27	139.35	10.79	2338.66
E-128	water supply to the hydrolysis of methylactate	96.83	100.00	LP-STEAM	167.00	143.11	0.10	9.43
E-134	water supply to filtration after enzymatic hydrolysis	17.24	20.76	Fermentation	47.83	45.00	0.68	132.35
E-136	Esterification	92.09	95.91	Condenser (distillation #2)	100.07	98.83	10.08	9749.54
E-120	water supply to filtration after precipitation	4.00	70.00	Condenser (distillation #1)	97.83	96.45	13.02	111.22
E-122	fermentation broth from fermentation, sent to precipitation	45.00	70.00	Condenser (distillation #1)	97.83	96.45	4.63	84.14

E-154	Reboiler (distillation #1)	100.28	100.28	Line 3_Dirty steam	135.07	135.01	0.12	33.81
E-152	water supply to filtration after enzymatic hydrolysis	4.00	5.63	LA cooling	42.93	30.00	0.32	6.10
E-140	crude LA produced from the precipitation, sent to the evaporation	77.56	85.66	Condenser (distillation #1)	95.58	93.56	17.89	289.24
E-139	water supply to filtration after fermentation	4.00	5.21	LA cooling	53.67	44.13	0.23	3.20
E-129	Reboiler (distillation #2)	100.32	101.67	LP-STEAM	167.00	143.11	46.60	4405.43
E-127	crude LA produced from the precipitation, sent to the evaporation	96.65	101.00	Dirty condensate	163.70	99.91	2.05	555.76
E-131	methanol supply to the esterification	20.00	95.91	Condenser (distillation #2)	100.07	98.83	6.13	1302.67
E-123	water supply to enzymatic hydrolysis	20.00	50.00	Condenser (distillation #1)	97.83	96.45	2.15	17.88
E-125	Reboiler (distillation #2)	100.32	101.67	Line 3_Dirty steam	149.27	139.35	11.81	1375.03
E-153	crude LA produced from the precipitation, sent to the evaporation	69.47	76.44	Condenser (distillation #1)	93.33	90.15	14.32	149.72
E-151	crude LA produced from the precipitation, sent to the evaporation	76.44	77.56	LP-STEAM	113.75	110.00	2.30	337.27
E-145	Reboiler (distillation #1)	100.28	100.81	LP-STEAM	143.11	113.75	74.24	29595.97
E-149	Hydrolysis	100.00	100.50	LP-STEAM	113.75	110.00	6.54	5675.92
E-130	crude LA produced from the precipitation, sent to the evaporation	96.65	101.00	LP-STEAM	167.00	143.11	13.70	1285.15
E-132	water supply to the hydrolysis of methylactate	74.24	96.83	Condenser (distillation #2)	100.07	98.83	0.73	22.29
E-124	methanol supply to the esterification	95.91	100.00	Line 3_Dirty steam	149.27	139.35	0.33	71.59
E-118	water supply to filtration after enzymatic hydrolysis	20.76	50.00	LA cooling	101.00	53.67	1.24	20.29
Sum							307.25	62639.71

Table C 3 Integrated bio-based lactic acid plant with the recovery by electrodialysis in scenario 1 (IFBR B, Scenario 1)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-115	heating for the reboiler at distillation #1	100.32	100.81	LP-STEAM	164.41	152.97	51.31	8856.10
E-119	heating for the reboiler at distillation #2	100.37	101.46	LP-STEAM	152.97	110.00	56.28	22869.62
E-121	LA separated by electrodialysis, sent to the evaporation	95.88	101.00	LP-STEAM	152.97	110.00	127.74	12970.37
E-113	heating for the esterification	92.29	92.59	Dirty condensate	115.85	97.87	0.51	418.11
E-114	heating for the reboiler at distillation #1	100.32	100.81	Line 3_Dirty steam	149.27	135.08	32.81	7963.52
E-118	heating for the hydrolysis of methylactate	100.00	100.50	LP-STEAM	152.97	110.00	8.49	3334.40
E-120	heating for the enzymatic hydrolysis	50.00	50.50	LP-STEAM	152.97	110.00	0.16	19.71
E-110	methanol supply to the esterification	95.85	100.00	Dirty condensate	163.70	115.85	0.33	91.07
E-117	water supply to the hydrolysis of methylactate	95.85	100.00	LP-STEAM	152.97	110.00	0.10	34.42
E-111	heating for the esterification	92.59	100.00	Dirty condensate	163.70	115.85	1.20	312.42
E-109	heating for the esterification	92.59	100.00	LP-STEAM	167.00	164.41	11.63	1677.73
E-122	heating for the reboiler at distillation #1	100.32	100.32	Line 3_Dirty steam	135.08	135.01	0.15	43.75
Sum							290.73	58591.22

Table C 4 Integrated bio-based lactic acid plant with the recovery by electrodialysis in scenario 2 (IFBR B, Scenario 2)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-131	water supply to filtration after enzymatic hydrolysis	20.00	50.00	Condenser (distillation #1)	97.74	90.21	5.81	44.12
E-138	water supply to filtration after enzymatic hydrolysis	9.93	20.00	Fermentation	48.74	45.00	1.95	327.21
E-158	water supply to filtration after enzymatic hydrolysis	4.00	9.93	LA cooling	63.02	30.00	1.15	18.22
E-130	water supply to filtration after fermentation	22.73	45.00	Condenser (distillation #1)	97.74	90.21	4.29	31.85
E-149	water supply to filtration after fermentation	11.08	22.73	Dirty condensate	99.85	30.00	2.25	318.05
E-154	water supply to filtration after fermentation	4.00	11.08	LA cooling	100.16	63.02	1.37	10.69
E-126	heating for the esterification	96.38	100.00	LP-STEAM	167.00	134.19	1.60	316.17
E-135	heating for the esterification	96.38	100.00	Line 3_Dirty steam	149.27	138.69	10.41	2285.54
E-139	heating for the esterification	92.69	96.38	Condenser (distillation #2)	99.62	99.45	12.24	13024.02
E-160	heating for the esterification	92.29	92.69	LP-STEAM	110.30	110.00	1.34	757.71
E-140	water supply to the hydrolysis of methylactate	97.00	100.00	Dirty condensate	120.03	117.00	0.10	24.97
E-143	water supply to the hydrolysis of methylactate	96.22	97.00	LA cooling	101.00	100.33	0.03	2.35
E-146	water supply to the hydrolysis of methylactate	20.36	96.22	Condenser (distillation #2)	99.45	99.25	2.46	16.07
E-153	water supply to the hydrolysis of methylactate	20.00	20.36	LA cooling	100.16	63.02	0.01	0.07
E-133	water supply to enzymatic hydrolysis	20.00	50.00	Condenser (distillation #1)	97.74	90.21	2.18	15.09
E-156	heating for the enzymatic hydrolysis	50.00	50.50	LP-STEAM	128.70	110.30	0.16	22.71
E-159	heating for the hydrolysis of methylactate	100.00	100.50	Line 3_Dirty steam	138.69	135.01	8.49	2321.45
E-128	LA separated by electrodialysis, sent to the evaporation	100.18	101.00	LP-STEAM	167.00	134.19	111.37	11618.19
E-136	LA separated by electrodialysis, sent to the evaporation	100.18	101.00	Dirty condensate	163.70	120.03	1.40	190.06

E-137	LA separated by electrodialysis, sent to the evaporation	100.18	101.00	Line 3_Dirty steam	149.27	138.69	13.73	1597.39
E-142	LA separated by electrodialysis, sent to the evaporation	96.22	100.18	LP-STEAM	134.19	128.72	0.60	93.56
E-144	LA separated by electrodialysis, sent to the evaporation	96.22	100.18	Dirty condensate	117.00	99.85	0.55	379.31
E-145	LA separated by electrodialysis, sent to the evaporation	73.40	96.22	LP-STEAM	128.72	128.70	0.10	11.93
E-147	LA separated by electrodialysis, sent to the evaporation	73.40	96.22	Condenser (distillation #2)	99.45	99.25	6.50	147.41
E-148	LA separated by electrodialysis, sent to the evaporation	73.40	96.22	LA cooling	100.33	100.16	0.01	0.24
E-152	LA separated by electrodialysis, sent to the evaporation	45.00	73.40	Condenser (distillation #2)	99.25	98.25	8.22	53.79
E-134	methanol supply to the esterification	95.85	100.00	Line 3_Dirty steam	149.27	138.69	0.33	73.08
E-150	methanol supply to the esterification	20.00	95.85	Condenser (distillation #2)	99.25	98.25	6.13	1303.22
E-127	heating for the reboiler at distillation #1	100.65	100.81	LP-STEAM	167.00	134.19	1.88	391.44
E-155	heating for the reboiler at distillation #1	100.32	100.65	LP-STEAM	128.70	110.30	82.37	47256.83
E-161	heating for the reboiler at distillation #1	100.32	100.32	LP-STEAM	110.30	110.00	0.02	24.93
E-125	heating for the reboiler at distillation #2	100.54	101.46	LP-STEAM	167.00	134.19	32.35	3424.80
E-141	heating for the reboiler at distillation #2	100.37	100.54	LP-STEAM	134.19	128.72	23.94	3888.15
sum							345.32	89990.60

Table C 5 Integrated bio-based succinic acid plant with the recovery by direct crystallization in scenario 1 (IFBR C, Scenario 1)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-115	crude SA produced from the fermentation, sent to the evaporation	37.00	37.03	Line 3_Dirty steam	135.07	135.01	0.12	11.99
E-107	water supply to filtration after fermentation	4.00	37.00	Dirty condensate	163.70	30.00	1.15	207.60
E-106	water supply to filtration after fermentation	4.00	37.00	LP-STEAM	167.00	166.37	2.91	200.21
E-108	water supply to filtration after enzymatic hydrolysis	4.00	15.27	Dirty condensate	163.70	30.00	2.18	329.20
E-110	crude SA produced from the fermentation, sent to the evaporation	37.03	102.00	LP-STEAM	166.37	111.15	257.36	43341.64
E-111	crude SA produced from the fermentation, sent to the evaporation	37.03	102.00	Line 3_Dirty steam	149.27	135.07	32.85	4883.34
E-109	air sent to dryer	4.00	100.00	Dirty condensate	163.70	30.00	0.96	285.81
E-113	heating for the evaporation	102.00	102.50	LP-STEAM	111.15	110.00	1.60	1921.14
E-114	heating for the enzymatic hydrolysis	50.00	50.50	LP-STEAM	111.15	110.00	0.61	101.85
E-112	water supply to filtration after enzymatic hydrolysis	33.75	50.00	LP-STEAM	111.15	110.00	3.15	460.35
Sum							302.89	51743.13

Table C 6 Integrated bio-based succinic acid plant with the recovery by direct crystallization in scenario 2 (IFBR C, Scenario 2)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-122	water supply to filtration after enzymatic hydrolysis	4.00	23.67	sugars cooling, sent to fermentation	50.00	37.00	3.58	69.03
E-124	water supply to filtration after enzymatic hydrolysis	4.00	23.67	air from dryer	43.62	27.40	0.23	14.96
E-117	water supply to filtration after enzymatic hydrolysis	23.67	50.00	LP-STEAM	167.00	110.68	5.10	273.73
E-123	water supply to filtration after fermentation	4.00	9.38	air from dryer	43.62	27.40	1.03	45.30
E-120	water supply to filtration after fermentation	9.38	37.00	Dirty condensate	163.70	30.00	4.30	440.55
E-114	water supply to filtration after fermentation	9.38	37.00	air from dryer	64.27	43.62	0.99	40.26
E-130	air sent to dryer	4.00	100.00	LP-STEAM	110.68	110.00	0.96	3212.87
E-127	water supply to enzymatic hydrolysis	4.00	15.75	air from dryer	26.64	7.24	0.84	239.47
E-115	water supply to enzymatic hydrolysis	15.75	50.00	air from dryer	64.27	43.62	2.46	161.32
E-132	heating for the enzymatic hydrolysis	50.00	50.50	LP-STEAM	110.68	110.00	0.61	102.25
E-121	crude SA produced from the fermentation, sent to the evaporation	37.00	102.00	Line 3_Dirty steam	149.27	135.01	32.96	3963.90
E-118	crude SA produced from the fermentation, sent to the evaporation	37.00	102.00	LP-STEAM	167.00	110.68	257.36	42019.71
E-131	heating for the evaporation	102.00	102.50	LP-STEAM	110.68	110.00	1.60	1974.86
sum							312.02	52558.19

Table C 7 Integrated bio-based succinic acid plant with the recovery by electrodialysis in scenario 1 (IFBR D, Scenario 1)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-115	water supply to enzymatic hydrolysis	4.00	5.50	Dirty condensate	33.35	30.00	0.11	40.08
E-108	water supply to enzymatic hydrolysis	5.50	50.00	Dirty condensate	163.70	33.35	3.19	616.90
E-110	SA produced from the electrodialysis, sent to the evaporation	37.03	102.00	LP-STEAM	166.30	110.31	202.16	34440.41
E-107	water supply to filtration after enzymatic hydrolysis	13.35	50.00	LP-STEAM	167.00	166.30	2.52	187.90
E-111	air sent to dryer	4.00	100.00	Line 3_Dirty steam	149.27	135.07	0.96	119.36
E-109	water supply to filtration after enzymatic hydrolysis	13.35	50.00	Dirty condensate	163.70	33.35	1.00	214.87
E-113	heating for the evaporation	102.00	102.50	LP-STEAM	110.31	110.00	0.96	1212.34
E-116	SA produced from the electrodialysis, sent to the evaporation	37.00	37.03	Line 3_Dirty steam	135.07	135.01	0.12	11.99
E-114	heating for the enzymatic hydrolysis	50.00	50.50	LP-STEAM	110.31	110.00	0.16	26.10
E-112	SA produced from the electrodialysis, sent to the evaporation	37.03	102.00	Line 3_Dirty steam	149.27	135.07	31.88	4740.36
Sum							243.06	41610.30

Table C 8 Integrated bio-based succinic acid plant with the recovery by electrodialysis in scenario 1 (IFBR D, Scenario 2)

No.	Cold Stream	Cold in [◦C]	Cold out [◦C]	Hot Stream	Hot in [◦C]	Hot out [◦C]	Load [MW]	Area [m^2]
E-129	water supply to filtration after enzymatic hydrolysis	4.00	12.02	Fermentation	37.44	37.00	0.78	141.86
E-130	water supply to filtration after enzymatic hydrolysis	4.00	12.02	air from dryer	28.45	7.24	0.78	220.98
E-122	water supply to filtration after enzymatic hydrolysis	12.02	50.00	LP-STEAM	167.00	110.58	2.52	128.37
E-119	water supply to filtration after enzymatic hydrolysis	12.02	50.00	air from dryer	69.71	28.45	4.83	528.22
E-120	water supply to filtration after fermentation	17.98	37.00	sugars cooling, sent to fermentation	50.00	45.85	1.14	33.65
E-128	water supply to filtration after fermentation	4.39	17.98	Fermentation	37.44	37.00	1.73	362.15
E-134	water supply to filtration after fermentation	4.04	4.39	sugars cooling, sent to fermentation	45.85	37.00	0.07	1.01
E-132	water supply to filtration after fermentation	4.39	17.98	Dirty condensate	57.00	30.00	0.87	154.84
E-140	water supply to filtration after fermentation	4.00	4.04	Fermentation	37.00	37.00	0.01	1.20
E-125	water supply to filtration after fermentation	17.98	37.00	Dirty condensate	163.70	57.00	2.50	191.70
E-137	air sent to dryer	4.00	100.00	LP-STEAM	110.58	110.00	0.96	3220.51
E-126	water supply to enzymatic hydrolysis	37.00	50.00	Dirty condensate	163.70	57.00	0.93	99.24
E-135	water supply to enzymatic hydrolysis	4.00	37.00	sugars cooling, sent to fermentation	45.85	37.00	2.37	80.46
E-139	heating for the enzymatic hydrolysis	50.00	50.50	LP-STEAM	110.58	110.00	0.16	26.04
E-127	SA produced from the electrodialysis, sent to the evaporation	37.00	102.00	Line 3_Dirty steam	149.27	135.01	32.96	3967.43
E-123	SA produced from the electrodialysis, sent to the evaporation	37.00	102.00	LP-STEAM	167.00	110.58	201.20	33009.94
E-138	heating for the evaporation	102.00	102.50	LP-STEAM	110.58	110.00	0.96	1192.58
sum							254.77	43360.18

APPENDIX D – CAPITAL COSTS

The equipment costs for the production of lactic and succinic acid are estimated according to a power law of capacity in Eq D.1 [110]:

$$C_E = C_B \left(\frac{Q}{Q_B}\right)^M \qquad \text{(Eq D.1)}$$

Whereby:

C_E = equipment cost with capacity Q

C_B = base cost for equipment with capacity Q_B

M = constant depending on equipment type

C_B, Q_B, and M are obtained from the literature [3, 55], Q is obtained from the Aspen Plus simulation results. To calculate the total capital cost of equipment, an installation factor from the literature [55] and the number of equipment are multiplied. Because published data of equipment cost are often old, such data were brought up-to-date using cost indexes using Eq. D.2 [110]:

$$\frac{C_1}{C_2} \qquad \text{(Eq. D.2)}$$

Whereby:

C_1 = equipment cost in year 1

C_2 = equipment cost in year 2

$INDEX_1$ = cost index in year 1

$INDEX_2$ = cost index in year 2

Chemical Engineering (CE) Index is used to update literature data to year 2012.

The HEX costs are calculated based on the following generic formula [111]:

$$C_{HEX} = C_B F_D F_P F_M \qquad \text{(Eq. D.3)}$$

Whereby:

C_B is assumed to be base cost for carbon steel floating head heat exchanger:

$$C_B = exp^{\{8.202+0.01506(\ln A)+0.06811(\ln A)^2\}} \qquad \text{(Eq. D.4)}$$

F_D is a design factor depending on the heat exchanger design or type:

$$F_D = exp^{\{-0.9003+0.0906(\ln A)\}} \qquad \text{(Eq. D.5)}$$

F_P is the design-pressure factor (4200 ~ 6200 kN/m^2):

$$F_P = 1.4272 + 0.12088\ (\ln A) \qquad \text{(Eq. D.6)}$$

F_M is the material cost factor for stainless steel 316:

$$F_M = 1.4144 + 0.23296\ (\ln A) \qquad \text{(Eq. D.7)}$$

Table D 1 HEX installation

	HEX cost [$]		Pipe and installation [$]		Sum [$]	
	Scenario 1	Scenario 2	Scenario 1	Scenario 2	Scenario 1	Scenario 2
IFBR A	73,750,371	58,054,444	22,125,111	17,416,333	95,875,483	75,470,777
IFBR B	96,047,638	80,416,212	28,814,291	24,124,864	124,861,930	104,541,076
IFBR C	157,417,894	158,078,195	47,225,368	47,423,459	204,643,262	205,501,654
IFBR D	112,473,410	114,490,675	33,742,023	34,347,202	146,215,433	148,837,877

Table D 2 Installed equipment costs for the integrated bio-based lactic acid plant with the recovery by precipitation (IFBR A)

Unit	Quantity	Base Eq. cost (C_B)	Scaled on	Scaling Factor (M)	Installation Factor	Size Ratio (Q/Q_B)	Eq.cost (base year)	Base year	current year	Index (base year)	current year	Eq. cost (2012)	Capital Cost (2012)
Reactor	5	2,466,955											4,443,179
Enzymatic Hydrolysis	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Fermentation	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Precipitation	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Esterification	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Hydrolysis	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Filtration	3	100,000	Flow	0.6	1.25	1	125,000	2000	2012	394.1	584.6	185,422	556,267
Evaporation	2	435,650	Area	0.68	2.1	1.7	1,312,388	1996	2012	381.7	584.6	2,010,013	4,020,027
Distillation	2	478,100	Diameter	0.7	2.1	1.13	1,093,687	1998	2012	389.5	584.6	1,641,513	3,283,026
sum													**12,302,499**
HEX (Scenario 1)													95,875,483
HEX (Scenario 2)													75,470,777
Sum (Scenario 1)													**108,177,982**
Sum (Scenario 2)													**87,773,276**

Table D 3 Installed equipment costs for the integrated bio-based lactic acid plant with the recovery by electrodialysis (IFBR B)

Unit	Quantity	Base Eq. cost (C_B)	Scaled on	Scaling Factor (M)	Installation Factor	Size Ratio (Q/Q_B)	Eq.cost (base year)	Base year	current year	Index (base year)	current year	Eq. cost (2012)	Capital Cost (2012)
Reactor	5	1,984,094											3,570,138
Enzymatic Hydrolysis	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Fermentation	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Electrodialysis	1	10,530	Flow	0.6	1.2	0.736	10,513	2000	2012	394.1	584.6	15,595	15,595
Esterification	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Hydrolysis	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Filtration	3	100,000	Flow	0.6	1.25	1	125,000	2000	2012	394.1	584.6	185,422	556,267
Evaporation	2	435,650	Area	0.68	2.1	1.7	1,312,388	1996	2012	381.7	584.6	2,010,013	4,020,027
Distillation	2	478,100	Diameter	0.7	2.1	1.13	1,093,687	1998	2012	389.5	584.6	1,641,513	3,283,026
sum													**11,429,458**
HEX (Scenario 1)													124,861,930
HEX (Scenario 2)													104,541,076
Sum (Scenario 1)													**136,291,388**
Sum (Scenario 2)													**115,970,534**

Table D 4 Installed equipment costs for the integrated bio-based succinic acid plant with the recovery by direct crystallization (IFBR C)

Unit	Quantity	Base Eq. cost (C_B)	Scaled on	Scaling Factor (M)	Installation Factor	Size Ratio (Q/Q_B)	Eq.cost (base year)	Base year	current year	Index (base year)	current year	Eq. cost (2012)	Capital Cost (2012)
Reactor	2	986,782											1,777,272
Enzymatic Hydrolysis	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Fermentation	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Filtration	1	100,000	Flow	0.6	1.25	1	125,000	2000	2012	394.1	584.6	185,422	185,422
Evaporation	1	435,650	Area	0.68	2.1	1.7	1,312,388	1996	2012	381.7	584.6	2,010,013	2,010,013
Crystallization	1	300,000	Flow	0.6	1.2	1	360,000	1990	2012	357.6	584.6	588,523	588,523
Dryer	1	15,498	Flow	0.6	1.3	0.61	14,977	1999	2012	390.6	584.6	22,415	22,415
sum													**4,583,646**
HEX (Scenario 1)													204,643,262
HEX (Scenario 2)													205,501,654
Sum (Scenario 1)													**209,226,908**
Sum (Scenario 2)													**210,085,300**

Table D 5 Installed equipment costs for the integrated bio-based succinic acid plant with the recovery by electrodialysis (IFBR D)

Unit	Quantity	Base Eq. cost (C_B)	Scaled on	Scaling Factor (M)	Installation Factor	Size Ratio (Q/Q_B)	Eq.cost (base year)	Base year	current year	Index (base year)	current year	Eq. cost (2012)	Capital Cost (2012)
Reactor	2	986,782											1,777,272
Enzymatic Hydrolysis	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Fermentation	1	493,391	Flow	0.6	1.2	1	592,069	1998	2012	389.5	584.6	888,636	888,636
Filtration	1	100,000	Flow	0.6	1.25	1	125,000	2000	2012	394.1	584.6	185,422	185,422
Evaporation	1	435,650	Area	0.68	2.1	1.7	1,312,388	1996	2012	381.7	584.6	2,010,013	2,010,013
Crystallization	1	300,000	Flow	0.6	1.2	1	360,000	1990	2012	357.6	584.6	588,523	588,523
Electrodialysis	1	10,530	Flow	0.6	1.2	0.616	9,448	1984	2012	322.7	584.6	17,117	17,117
Dryer	1	15,498	Flow	0.6	1.3	0.61	14,977	1999	2012	390.6	584.6	22,415	22,415
sum													4,600,763
HEX (Scenario 1)													146,215,433
HEX (Scenario 2)													148,837,877
Sum (Scenario 1)													150,816,196
Sum (Scenario 2)													153,438,640

APPENDIX E – ANNUAL OPERATING COSTS

Table E 1 various annual operating costs for the integrated bio-based lactic acid plant with the recovery by precipitation (IFBR A)

	uses		unit cost		cost	
Feedstock	500	ton/day	0	$/ton	-	$/day
Enzyme	10	ton/day	0.0552	$/lb	1,217	$/day
Microorganism	13	ton/day	0.025	$/kg	324	$/day
Nutrient	64	ton/day	0.0804	$/lb	11,344	$/day
Ca(OH)2	118	ton/day	0.0348	$/lb	9,053	$/day
H2SO4	173	ton/day	0.0124	$/lb	4,729	$/day
Gypsum disposal	241	ton/day	0.0094	$/lb	4,994	$/day
MeOH	0.12	ton/day	330	$/ton	39	$/day
LP-steam (Scenario 1)	143	MW	0.007	$/MJ	86,702	$/day
LP-steam (Scenario 2)	144	MW	0.007	$/MJ	87,176	$/day
Sum (Scenario 1)					118,403	$/day
Sum (Scenario 2)					118,877	$/day
Sum (Scenario 1)					**13,813,789**	**$/year**
Sum (Scenario 2)					**13,869,062**	**$/year**

Table E 2 Fixed annual operating costs for the integrated bio-based lactic acid plant with the recovery by precipitation (IFBR A)

	Unit cost	people	Scenario 1	Scenario 2	
Plant Manager	80000	1	80,000	80,000	$/year
Plant Engineer	65000	1	65,000	65,000	$/year
Maintenance Supervisor	60000	1	60,000	60,000	$/year
Lab Manager	50000	1	50,000	50,000	$/year
Shift Supervisor	37000	5	185,000	185,000	$/year
Lab Technician	25000	2	50,000	50,000	$/year
Maintenance Technician	28000	8	224,000	224,000	$/year
Shift Operators	25000	20	500,000	500,000	$/year
Yard Employees	20000	32	640,000	640,000	$/year
General Manager	100000	1	100,000	100,000	$/year
Clerks & Secretaries	20000	5	100,000	100,000	$/year
Total Salaries (1998 $)			2,054,000	2,054,000	$/year
Total Salaries (2015 $)			3,116,523	3,116,523	$/year
Final			1,558,261	1,558,261	$/year
General Overhead	60%	Of Total Salaries	934,957	934,957	$/year
Maintenance	2%	Of Installed Equipment Cost	2,163,560	1,755,466	$/year
Insurance & Taxes	1.5%	Of Installed Equipment Cost	1,622,670	1,316,599	$/year
Sum			**6,279,447**	**5,565,283**	**$/year**

Table E 3 Various annual operating costs for the integrated bio-based lactic acid plant with the recovery by electrodialysis (IFBR B)

	uses		unit cost		cost	
Feedstock	500	tonne/day	0		-	$/day
Enzyme	10	tonne/day	0.0552	$/lb	1,217	$/day
Microorganism	0.036	tonne/day	0.025	$/kg	1	$/day
Nutrient	64	tonne/day	0.08	$/lb	11,344	$/day
NaOH	1.42	tonne/day	400	$/ton	569	$/day
MeOH	0.12	tonne/day	330	$/ton	39	$/day
Membrane replace			439	$/year	1	$/day
Electricity usage	0.88	kWh/kg LA	0.0796	¢/kWh	14,646	$/day
LP-steam (Scenario 1)	256	MW	0	$/MJ	154,654	$/day
LP-steam (Scenario 2)	256	MW	0	$/MJ	154,654	$/day
Sum (Scenario 1)					167,825	$/day
Sum (Scenario 2)					167,825	$/day
Sum (Scenario 1)					**19,581,627**	**$/year**
Sum (Scenario 2)					**19,581,637**	**$/year**

Table E 4 Fixed annual operating costs for the integrated bio-based lactic acid plant with the recovery by electrodialysis (IFBR B)

	Salary	people	Scenario 1	Scenario 2	
Plant Manager	80000	1	80,000	80,000	$/year
Plant Engineer	65000	1	65,000	65,000	$/year
Maintenance Supervisor	60000	1	60,000	60,000	$/year
Lab Manager	50000	1	50,000	50,000	$/year
Shift Supervisor	37000	5	185,000	185,000	$/year
Lab Technician	25000	2	50,000	50,000	$/year
Maintenance Technician	28000	8	224,000	224,000	$/year
Shift Operators	25000	20	500,000	500,000	$/year
Yard Employees	20000	32	640,000	640,000	$/year
General Manager	100000	1	100,000	100,000	$/year
Clerks & Secretaries	20000	5	100,000	100,000	$/year
Total Salaries (1998 $)			2,054,000	2,054,000	$/year
Total Salaries (2015 $)			3,116,523	3,116,523	$/year
Final			1,558,261	1,558,261	$/year
General Overhead	60%	Of Total Salaries	934,957	934,957	$/year
Maintenance	2%	Of Installed Equipment Cost	2,725,828	2,319,411	$/year
Insurance & Taxes	2%	Of Installed Equipment Cost	2,044,371	1,739,558	$/year
Sum			**7,263,408**	**6,552,187**	**$/year**

Table E 5 Various annual operating costs for the integrated bio-based succinic acid plant with the recovery by direct crystallization (IFBR C)

	Use		Unit cost		Cost	
Feedstock	500	ton/day	0		-	$/day
Enzyme	10	ton/day	0.0552	$/lb	1,217	$/day
Microorganism	0.036	ton/day	0.025	$/kg	1	$/day
Nutrient	64	ton/day	0.0804	$/lb	11,344	$/day
NaOH	9.85	ton/day	0.0348	$/lb	756	$/day
LP-steam (Scenario 1)	266	MW	0	$/MJ	160,653	$/day
LP-steam (Scenario 2)	266	MW	0	$/MJ	160,653	$/day
Sum (Scenario 1)					173,971	$/day
Sum (Scenario 2)					173,971	$/day
Sum (Scenario 1)					**20,296,563**	**$/year**
Sum (Scenario 2)					**20,296,563**	**$/year**

Table E 6 Fixed annual operating costs for the integrated bio-based succinic acid plant with the recovery by direct crystallization (IFBR C)

	Salary	people	Scenario 1	Scenario 2	
Plant Manager	80000	1	80,000	80,000	$/year
Plant Engineer	65000	1	65,000	65,000	$/year
Maintenance Supervisor	60000	1	60,000	60,000	$/year
Lab Manager	50000	1	50,000	50,000	$/year
Shift Supervisor	37000	5	185,000	185,000	$/year
Lab Technician	25000	2	50,000	50,000	$/year
Maintenance Technician	28000	8	224,000	224,000	$/year
Shift Operators	25000	20	500,000	500,000	$/year
Yard Employees	20000	32	640,000	640,000	$/year
General Manager	100000	1	100,000	100,000	$/year
Clerks & Secretaries	20000	5	100,000	100,000	$/year
Total Salaries (1998 $)			2,054,000	2,054,000	$/year
Total Salaries (2015 $)			3,116,523	3,116,523	$/year
Final			1,558,261	1,558,261	$/year
General Overhead	60%	Of Total Salaries	934,957	934,957	$/year
Maintenance	2%	Of Installed Equipment Cost	4,184,538	4,201,706	$/year
Insurance & Taxes	2%	Of Installed Equipment Cost	3,138,404	3,151,280	$/year
Sum			**9,816,160**	**9,846,204**	**$/year**

Table E 7 Various annual operating costs for the integrated bio-based succinic acid plant with the recovery by electrodialysis (IFBR D)

	Use		Unit cost		Cost	
Feedstock	500	tonne/day	0		-	$/day
Enzyme	10	tonne/day	0.0552	$/lb	1,217	$/day
Microorganism	0.036	tonne/day	0.025	$/kg	1	$/day
Nutrient	64	tonne/day	0.0804	$/lb	11,344	$/day
NaOH	0.027	tonne/day	0.0348	$/lb	2	$/day
Membrane replace			439	$/year	1	$/day
Electricity usage	0.88	kWh/kg SA	0.0796	¢/kWh	12,258	$/day
LP-steam (Scenario 1)	206	MW	0	$/MJ	124,467	$/day
LP-steam (Scenario 2)	206	MW	0	$/MJ	124,467	$/day
Sum (Scenario 1)					149,291	$/day
Sum (Scenario 2)					149,291	$/day
Sum (Scenario 1)					**17,417,242**	**$/year**
Sum (Scenario 2)					**17,417,242**	**$/year**

Table E 8 Fixed annual operating costs for the integrated bio-based succinic acid plant with the recovery by electrodialysis (IFBR D)

	Salary	People	Scenario 1	Scenario 2	
Plant Manager	80000	1	80,000	80,000	$/year
Plant Engineer	65000	1	65,000	65,000	$/year
Maintenance Supervisor	60000	1	60,000	60,000	$/year
Lab Manager	50000	1	50,000	50,000	$/year
Shift Supervisor	37000	5	185,000	185,000	$/year
Lab Technician	25000	2	50,000	50,000	$/year
Maintenance Technician	28000	8	224,000	224,000	$/year
Shift Operators	25000	20	500,000	500,000	$/year
Yard Employees	20000	32	640,000	640,000	$/year
General Manager	100000	1	100,000	100,000	$/year
Clerks & Secretaries	20000	5	100,000	100,000	$/year
Total Salaries (1998 $)			2,054,000	2,054,000	$/year
Total Salaries (2015 $)			3,116,523	3,116,523	$/year
Final			934,957	934,957	$/year
General Overhead	60%	Of Total Salaries	560,974	560,974	$/year
Maintenance	2%	Of Installed Equipment Cost	3,016,324	3,068,773	$/year
Insurance & Taxes	2%	Of Installed Equipment Cost	2,262,243	2,301,580	$/year
Sum			**6,774,488**	**6,866,273**	**$/year**